Synthesis and complexation of Cyclopentadienes

Webber, David Hugh

Synthesis and Complexation of Cyclopentadienes

With a particular emphasis on cyclopentadienes bearing bulky hydrocarbyl substituents, linked bis(cyclopentadienes) and on aspects of chirality relating to cyclopentadienyl ligands and complexes.

Incorporating a useful chapter reviewing many synthetic approaches to cyclopentadienes and cyclopentadiene precursors.

A thesis submitted in part fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Durham.

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Ustinov College (formerly the Graduate Society)

February 2004

Statement of Copyright

Declaration

The work described in this thesis was carried out in the Department of Chemistry at the University of Durham between October 1999 and February 2003. All the work is my own, unless stated to the contrary, and it has not been submitted previously for a degree at this or any other University.

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The Engineering and Physical Sciences Research Council (EPSRC) is gratefully acknowledged for providing the grant without which this work would not have been possible.

Acknowledgements

I would like to thank all the staff in the Durham University Chemistry Department in general and my supervisor, Dr A.K. Hughes, in particular. Dr Hughes has been particularly helpful, not least by putting up with my long absences on health grounds with the utmost of good grace. I must also mention Dr H. Puschmann and C. Broder (in Prof. J.A.K. Howards' group) who were responsible for doing the crystallographic work.

Outside of the Chemistry Department, I must thank my girlfriend, then wife – the incomparable Amy Keller (then Webber!). She has supported me in every way (not least financially!) during the writing of this thesis, which has been prolonged. The only problem is that now that the thesis is finished, I no longer have an excuse for having Amy cook, clean and generally run around after me!

I would like to un-acknowledge (if this is possible) my back which has given continual pain and discomfort throughout the duration of the PhD work, despite continual medical referrals.

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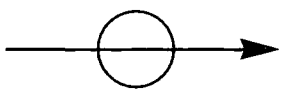
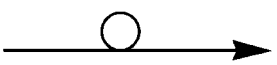
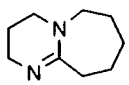


This type of arrow is used in chemical equations in this thesis (and elsewhere). The arrow merely indicates the redrawing of a structural formula, e.g. to show a mechanism more clearly; it does not indicate any chemical change. The redrawing could be as simple as a rotation of the original diagram. This arrow goes further than simply *implying* no chemical change between the two species it connects, it *explicitly indicates* that they are identical. **Note:** While some other writers use this very useful symbol similarly, it does not appear to be universally employed. Similar symbols may be met with which have different meanings. For example, the following arrow with conjoined circle was used by Rieke *et al*[*] to denote molecular rearrangements: 

=>	This symbol means *this implies*
b	Broad
bp	Boiling Point
ch	Chapter
CIP System	Cahn Ingold Prelog System. Also known as *CIP Rules*. A set of rules used in chemical nomenclature to assign relative priorities (*CIP Priorities*) to different substituent groups in a molecule. Once this is done, further rules can be applied to generate unambiguous chirality descriptors (e.g. *R* or *S*) or isomer descriptors (e.g. *E* or *Z*).
Class I – V ligands	Refer to the *ansa*- cyclopentadienyl classification system given in section 1.2.2
COSY	COrrelated SpectroscopY
Cp	Cyclopentadienyl
Cp#	Generalised cyclopentadienyl ligand, i.e. Cp, or substituted Cp with unspecified substituents.
Cp*	Pentamethylcyclopentadienyl

[*] R.D. Rieke, M.S. Sell, H. Xiong, *J. Am. Chem. Soc.*, **117**, 5429-5437, (1995)

$(Cp1)_2Fe$	*bis*-η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II)†
Cp1Cp2Fe	η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]-η^5-[1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II)†
$Cp1TiCl_3$	η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]trichlorotitanium(IV)†
$(Cp3)_2Fe$	*bis*-(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl)iron(II)†
CpH	Cyclopentadiene
d	Doublet
DBU	1,8-DiazaBicyclo[5.4.0]Undec-7-ene,  . A strong, non-nucleophillic base.
DEPT	Distortion Enhancement through Polarization Transfer
DMPU	N,N'-Dimethyl-N,N'-PropyleneUrea, also known as 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone. A highly polar, non-protic solvent.
d of d	Doublet of Doublets
d of t	Doublet of Triplets
EBI	Ethylene BisIndenyl
EBTHI	Ethylene Bis(TetraHydroIndenyl)
ed	Editor
eds	Editors
GC-FID	Gas Chromatograph employing a Flame Ionisation Detector
HCp1	Cyclopentadiene 1, 1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene†
HCp2	Cyclopentadiene 2, (*R,S*)-1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2*H*-indene†
HK1	Ketone 1, 3-methyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-one†
HMQC	Heteronuclear Multiple Quantum Coherence. (Sometimes referred to as ^1H-^{13}C COSY).
LDA	Lithium Diisopropyl Amide, $LiN(CH(CH_3)_2)_2$
LiK1	Lithiated Ketone 1†
Ln	Lanthanide
m	Multiplet
mp	Melting Point
p	Page

† Further information on the nomenclature of these compounds, including structural formulae, will be found in section 3.1. Some useful notes on the naming of hydroindene derivatives in general will be found in appendix 1.

pp	Page range
PE	Petroleum Ether, 40-60°C bp (Mostly hexane isomers)
PPA	Polyphosphoric acid.[‡]
PPA'	This abbreviation is used in this thesis to denote a specific concentration of polyphosphoric acid *viz* that which is equivalent to 115% H_3PO_4, i.e. 83.3% P_2O_5.[‡]
PS	Petroleum Spirit, 100-120°C bp
q	Quartet
rt	Room Temperature
s	Singlet
semiHCl	Semicarbazide HydroChloride
sh	Sharp
SPA	Concentrated H_3PO_4 at the standard lab concentration of 85% weight. SPA stands for Syrupy Phosphoric Acid, a term used in some old chemistry books.
t	triplet
THF	TetraHydroFuran
TMS	TetraMethylSilane. Note: When the abbreviation *TMS* is used as part of a larger chemical name or abbreviated chemical name, or is used as a label in a structural formula, it means *TriMethylSilyl*. For an example, see the entry for *TMSCp1*, below.
TMSCp1	(Trimethylsilyl)cyclopentadiene 1, (*R,S*)-1-(3,5-dimethylphenyl)-2-(trimethylsilyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene[†]

[‡] See appendix 2 for more details.
[†] See footnote on previous page.

Synthesis and Complexation of Cyclopentadienes

David Hugh Webber, Ustinov College (formerly the Graduate Society), Feb. 2004

Abstract:

The first part of chapter 1 gives a short general introduction to the importance of cyclopentadienyl complexes. This leads on to a presentation of the importance of chirality in cyclopentadienyl complexes with reference to their catalytic applications. The main bulk of the chapter then presents the subject of chirality in cyclopentadienyl complexes in terms of their molecular structure, with many important examples from the literature. There is also discussion of different methods of metallating cyclopentadienes and the influence of the choice of method on the ratio of stereoisomers produced.

Chapter 2 is a selective review of methods of synthesising cyclopentadienes and cyclopentadiene precursors (i.e. cyclopentenones and cyclopentenols). The review is biased towards syntheses which have been (or have the potential to be) used for the production of multigram batches of cyclopentadienes (and cyclopentadiene precursors) with structures of interest to organometallic chemists.

Chapter 3 presents the experimental work. The results are discussed first, after which the experimental procedures are presented.
The aliphatic Friedel-Crafts/Nazarov reaction between crotonic acid and cyclohexene in warm polyphosphoric acid is an established method of synthesising 3-methyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-one (HK1). The technique has been improved by adding a semicarbazone formation-hydrolysis purification step to remove the inevitable cyclohexyl crotonate byproduct.
1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene (HCp1) was prepared from 3-methyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-one (HK1) by the use of 3,5-dimethylphenyl magnesium bromide in THF. HCp1 was highly convenient on account of its crystallinity and was used to make metal complexes either by deprotonation and reaction with a metal chloride ($FeCl_2$) or through prior conversion to (*R,S*)-1-(3,5-dimethylphenyl)-2-(trimethylsilyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene (TMSCp1). The latter compound reacted readily with $ZrCl_4$, $TiCl_4$ and $NbCl_5$, although only the reaction with $TiCl_4$ lead to a isolable compound, η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]trichlorotitanium(IV) (Cp1$TiCl_3$).
The reaction of deprotonated HCp1 with $FeCl_2$ produced two ferrocenes, a major product, *bis*-η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II) (Cp1$_2$Fe), and a minor product, η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]-η^5-[1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II) (Cp1Cp2Fe). The minor product was thought to derive from some unknown impurity in the starting materials.
Crystal structures of TMSCp1 and Cp1Cp2Fe were obtained. The molecular structure of the latter is discussed.
To finish chapter 3, a proposal is outlined for a novel phosphonium salt/phosphorus ylid based approach to the synthesis of cyclopentadienes. The proposed reactions were not carried out, but it is hoped that a future investigator will conduct experiments in this area.

Appendix 1 gives some useful information on the naming of substituted hydroindenes.

Appendix 2 presents information and calculations on the composition of polyphosphoric acid. It also gives a method of making polyphosphoric acid in the lab.

Appendix 3 gives the crystal structure of TMSCp1 ((*R,S*)-1-(3,5-dimethylphenyl)-2-(trimethylsilyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene)

Appendix 4 gives the crystal structure of Cp1Cp2Fe (η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]-η^5-[1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II))

References for each chapter are collected together at the end of the chapter. References for the collected appendices are to be found at the very rear of the thesis.

1 Introduction and background

1.1 General introduction: the importance of the subject

The project here presented is concerned with the synthesis, structure and reactivity of transition metal and lanthanide complexes of novel chiral and prochiral cyclopentadienes sporting bulky hydrocarbyl substituents. The synthesis and study of these compounds is an area of chemistry which has been attracting great academic and industrial interest for some years, with the literature on the subject being extensive and continuing to expand rapidly. On the academic side, there is interest in the bonding, molecular structure, redox properties and many other characteristics of these compounds, while industry is excited by their catalytic abilities. Although certain catalytic processes involving metallocenes (viz. enantioselective hydrogenations, Diels - Alder reactions, epoxidations and several carbon – carbon bond forming reactions[1]) have not yet been developed sufficiently for industrial use[1], bulky metallocenes are of large and increasing importance in the manufacture of polyolefins.[2, 3]

From a study of the literature, it would appear to the present author that many of the chiral bulky substituted cyclopentadienyl complexes studied academically, and almost of those used industrially or being considered for possible industrial use, are based on titanium or zirconium[4]. There is, however, scope for using bulky substituted cyclopentadienyl complexes based on many other transition metals or on lanthanides. The lanthanide complexes in particular are attracting substantial academic interest, not least because of their value as experimental single component olefin polymerisation catalysts,[5, 6 and references therein] but also because there is scope for using the Lewis acidity of these compounds to effect the stereoselective catalysis of, for example, Diels – Alder reactions.[7] Also, it is possible that chiral Sm(II) metallocenes may be able to act as stoichiometric or catalytic stereospecific reducing agents. The possibilities of this area of chemistry are immense.

A useful paper on the bonding in bent metallocenes has recently been published.[8]

1.2 Introduction to chirality in metallocenes and half – sandwich compounds and the principles of chiral catalysis.

Useful introductions to stereochemical principles and terminology are available,[9 - 15] and an interesting article on early ideas of enantiomorphism, largely based of observations of the dissymmetric habit of certain crystalline substances but also discussing optically active molecules and methods of resolution, is also extant.[16]

A chiral molecule, or other object, is one which is not superimposable on its mirror image and can thus exist in two *enantiomeric* forms. Either enantiomer (in the absence of interactions with any other dissymmetric object) will be of equal energy and will interact with any given achiral object in a manner indistinguishable to the manner in which the other enantiomer will interact (indistinguishable, that is, to an achiral observer or an achiral third object). This indistinguishability would be lost if a given enantiomer of any other chiral object is also involved in the interaction in any way.

From the above statement, it can be inferred that to create an enantiomeric excess of a given enantiomer of a (given diastereomer of a) chiral product from a racemic, achiral or, in certain cases, homochiral substrate, one or more or the reagents and/or materials providing an environment for the reaction (i.e., solvents) must be chiral and enantiomerically enriched. In practical asymmetric syntheses the use of chiral solvents is normally not very effective and is expensive. A better method of achieving the desired chiral induction is often to use a chiral reagent or to modify the substrate by temporary attachment of a chiral auxiliary near the site of reaction, the auxiliary being a homochiral substance easy to prepare by resolution or derived from the chiral pool.* However, the most elegant method of directing the induction of chirality during a synthesis is to use a chiral catalyst; by this means a small amount of enantiopure material may produce an enantiomeric excess, very high in favourable cases, in a large amount of product. This is obviously a very favourable approach and a massive amount of industrial and academic work has, and continues to be, done with the aim of perfecting new catalyst systems and applying dissymmetric catalysts to new processes.[17]

Metallocenes, particularly those based on group 4 transition metals or lanthanides, are versatile catalysts which have been applied to many organic reactions. By the use of complexes containing chiral substituted cyclopentadienyl ligands many of these reactions may be rendered

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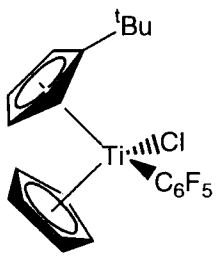
* The *chiral pool* is the reservoir of enantioenriched and enantiopure compounds present in and available from the biosphere.

enantioselective.[17 - 37] In addition, group 4 metallocenes are very effective [2, 38] and hence economically important olefin polymerisation catalysts.[2, 3] Lanthanum based metallocenes are also effective catalysts,[7] but have not yet received major industrial usage. Dissymmetric substituted metallocenes are used for the polymerisation of propene and other olefins which give side-chain-bearing polymers, because of their ability to control the stereochemistry of olefin insertion resulting in a product of regular tacticity.[5, 38, 39 - 54] Since the polymer chains have overall *meso* symmetry (to a very close approximation), a racemic catalyst gives essentially exactly the same results as one which is enantiopure, but by using an enantiopure metallocene catalyst to produce low molecular weight oligomers, chiral alkenes may be prepared.

Many of the first dissymmetric substituted cyclopentadienyl complexes had the metal as a chiral centre.[*, 55 - 61] Figure 1 shows a simple example of this type of complex.

Figure 1. An example of a cyclopentadienyl complex with the metal as a chiral centre[59]



Molecules of this type, while they can be synthesised from easily accessible ligands and may be academically interesting, are difficult to prepare in a non-racemic form.[32] Also, it would be expected that complexes of this form would be of limited use as enantioselective catalysts since ligand exchange could easily cause racemisation. However, cyclopentadienyl complexes with metal-based chirality, with or without additional chiral ligands, have been used as stoichiometric reagents in organic syntheses.[56, 60, 61]

More useful than complexes with metal-based chirality are those in which one or more of the cyclopentadienyl ligands are chiral, or have prochiral faces (Figure 2). Complexes of this type retain their dissymmetric properties even if the metal-ligand bond vectors should migrate around the metal during ligand exchange, oxidative addition or other reactions such as might take place during a catalytic cycle.

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[*] A complex is said to have *metal-based chirality* or is said to have the metal as a *chiral centre* if there is some rearrangement of metal-ligand bond vectors about the metal which can interconvert enantiomers or diastereomers. It must not be thought that chirality emanates from the metal, or any other axis, plane or centre of symmetry which may be referred to – these elements of chirality may be convenient to think about but they are abstract and rather arbitrary conceptions, chirality really being a property of the molecule in its entirety.

The requirement for a molecule to be chiral is that it should be devoid of any S_n symmetry elements.[10, 62] Looking at the substituted cyclopentadienyl anions shown in Figure 2a, assuming that that the substituents are achiral and free to rotate, it is easily seen that all the molecules possess a mirror plane coplanar with the paper; this is equivalent to saying that they have an S_1 axis perpendicular to the paper. Possession of such a symmetry element precludes dissymmetry, but the complexation of a metal fragment to one or the other *prochiral* faces destroys the mirror plane and results in a chiral molecule of low (C_1) symmetry. The choice of face determines the particular enantiomer produced; the faces are thus said to be *enantiotopic*.

If the disposition of achiral substituents around a cyclopentadienyl ring is such as to give both a mirror plane coplanar with the ring and a plane of symmetry perpendicular to this then the complexation of a (non chiral or prochiral) metal fragment to the ring will give rise to an achiral complex. An axially chiral compound could result if rotation of the cyclopentadienyl group around the ring-metal axis was impaired but the author is not aware that this has been observed in practice.*

If the stereochemistry of a cyclopentadienyl complex is not influenced by which face of the ligand is metallated then the faces are said to be *homotopic*. Clearly, the faces of any achiral, non-prochiral cyclopentadienyl ligand must be homotopic as an achiral complex results from metallation. However, a cyclopentadienyl ring substituted with one or, in certain cases, more than one freely-rotating chiral substituent, and which does not have overall *meso* symmetry, has homotopic faces and will give a chiral complex on metallation. In addition, C_2 symmetric annulated chiral cyclopentadienes are homotopically faced.

The two faces of any cyclopentadienyl ligand which is both chiral and prochiral give different diastereomers on metallation and are thus said to be *diastereotopic*.

As shown in Figure 2e, it is possible for cyclopentadienyl ligands to be propseudochiral and this interesting situation has been thoroughly investigated in the case of certain ferrocene derivatives.[63, 64] Due to constraints of space, pseudochirality will not be discussed further, apart from noting that it cannot be studied group-theoretically using standard point groups. However, by extending the usual list of symmetry operators by inclusion of the *chirality reversal* operator, a set of *pseudochirality groups* can be derived and used as the basis of a rigorous group-theoretical study.[65]

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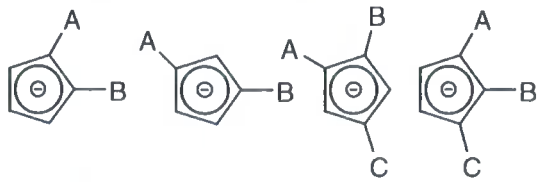
* R Baker may have made one, but the reference has not yet been found. See section 1.2.2.2.4 for a case which looks related on a casual glance as it involves an axially chiral ligand. The case is actually completely different because the final complex is not axially chiral, but instead has the features of a normal prochiral cyclopentadiene complex.

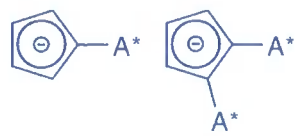
Figure 2. Chirality, prochirality and pro*pseudo*chirality in cyclopentadienyl ligands

a) Prochiral substituted cyclopentadienyl anions.
(Capital letters denote achiral substituents.)



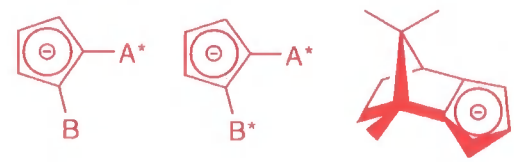
There are many other possible arrangements of achiral substituents around a cyclopentadienyl ring which will render its faces enantiotopic. The symmetry requirement for this is that there should be a mirror plane coplanar with the ring and no other symmetry elements.

b) Simple homotopically faced chiral cyclopentadienyl ligands.
(Starred capital letters indicate chiral substituents.)

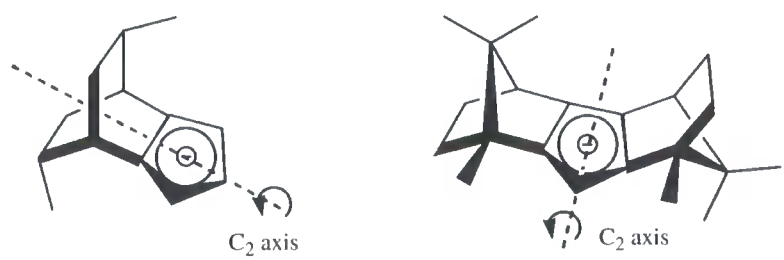


It is assumed that the substituents can rotate freely.

c) Diastereotopically faced cyclopentadienyl ligands. These are chiral while simultaneously possessing prochirality, the requirement for this being that there must be no symmetry elements present.

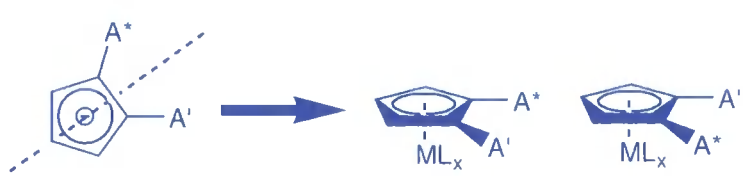


d) Homotopically faced chiral cyclopentadienyl ligands. These possess a C_2 axis coincident with the plane of the ring and have C_2 symmetry overall.



e) Propseudochiral diastereotopically faced cyclopentadienyl ligands. These are non-pseudochiral *meso* compounds exhibiting a mirror plane perpendicular to the plane of the ring and they give either one of two pseudoenantiomeric diastereomers on metallation.

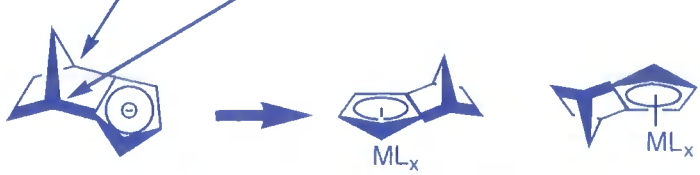
A* = chiral substituent
A' = chiral substituent, constitutionally identical to A*, but of opposite configuration



Mirror plane perpendicular to paper

Achiral pseudoenantiomeric meso diastereomers.

Chiral centres with opposite configuration giving overall *meso* symmetry



Achiral pseudoenantiomeric meso diastereomers.

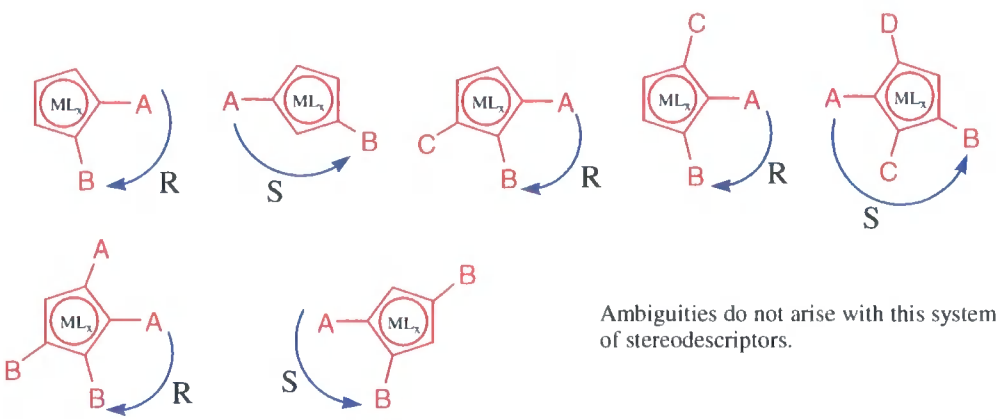
Figure 2 is continued on the next page

Figure 2 continued:

f) Chirality descriptors as applied to cyclopentadienyl complexes of prochiral ligands.

The diagrams show metallated Cp rings with the metal unit in front of the plane of the paper (i.e. the observer is looking down the metal-Cp axis from the metal twards the Cp unit). The CIP priorities of the substituents are ranked as follows: A>B>C>D.

The stereodescriptor is decided by considering the highest and second-highest priority substituents. (If there are multiple highest and/or second highest priority sustituents then the closest pair is used.) With the complex orientated as shown, an imaginary curved arrow is drawn round the ring along the shortest route from the highest to the second-highest priority substituent. The descriptor 'R' is applied to an arrow drawn in the clockwise sense and 'S' is used to denote the contrary situation. The diagrams make this clear.



Ambiguities do not arise with this system of stereodescriptors.

An alternative, but related system of assigning R or S configuration to Cp complexes has has been described*, but does not appear to be used any longer. In this system, one of the ring carbons (C-1) is assigned a configuration using the usual CIP rules with the metal atom being regarded as a singly-bonded substituent. In practice, the two systems will give the same stereodescriptor except when there are heavy-atom substituents bonded either directly to or one atom away from the ring.
* Ref: R.S.Cahn, C. Ingold, V. Prelog, *Specification of Molecular Chirality*, Angew. Chem. Int. Ed. Engl., **5**, 385-415 (partic. p394), (1966)

Cyclopentadienyl complexes in which the metal is a centre of pseudochirality are also known.[66]

1.2.1 Survey of non-linked chiral and prochiral cyclopentadienes

Chiral and prochiral cyclopentadienes and chiral cyclopentadienyl complexes have been reviewed.[4] One method which has been used to prepare enantiopure chiral substituted cyclopentadienyl ligands is to incorporate a substituent derived from the chiral pool; terpenes have been the most common choice.[18, 26, 32, 34, 36, 67 - 69] Homotopically faced homochiral substituted cyclopentadienes can be easily prepared from inexpensive terpenes, a typical synthesis being shown in Figure 3.[70] Alternatively, diastereotopically faced chiral annulated cyclopentadienes based on terpenes can be synthesised (Figure 4).[32, 34, 67, 69] These are more difficult to make and there are only a few examples.[32, 69] However, cyclopentadienes of this type do have advantages as chiral ligands, since they give complexes featuring a rigid dissymmetric environment around the metal and, while mixtures of diastereomers may be formed on metallation, separation of diastereomers is much easier than the resolution of enantiomers required for many other systems.

Figure 3. Simple preparation of an enantionpure homotopically faced chiral Cp ligand using a terpene as a substrate[70]

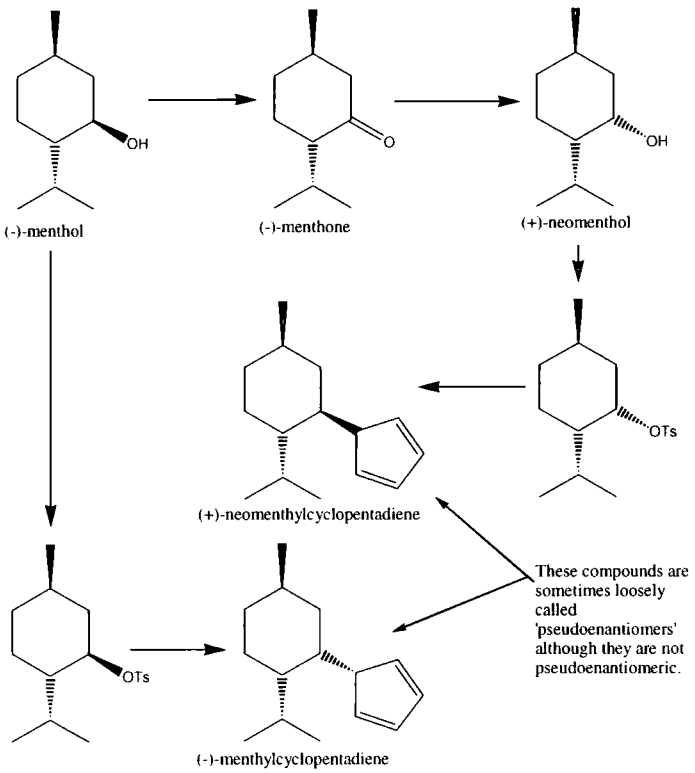


Figure 4. Formation of a C_1 symmetric annulated cyclopentadiene from a terpene[67]

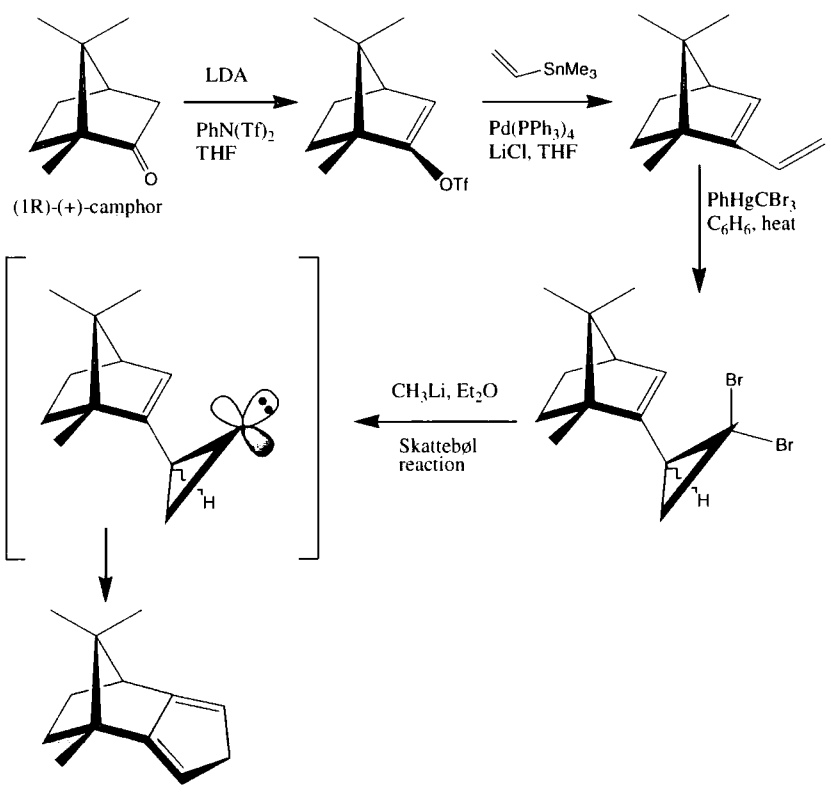
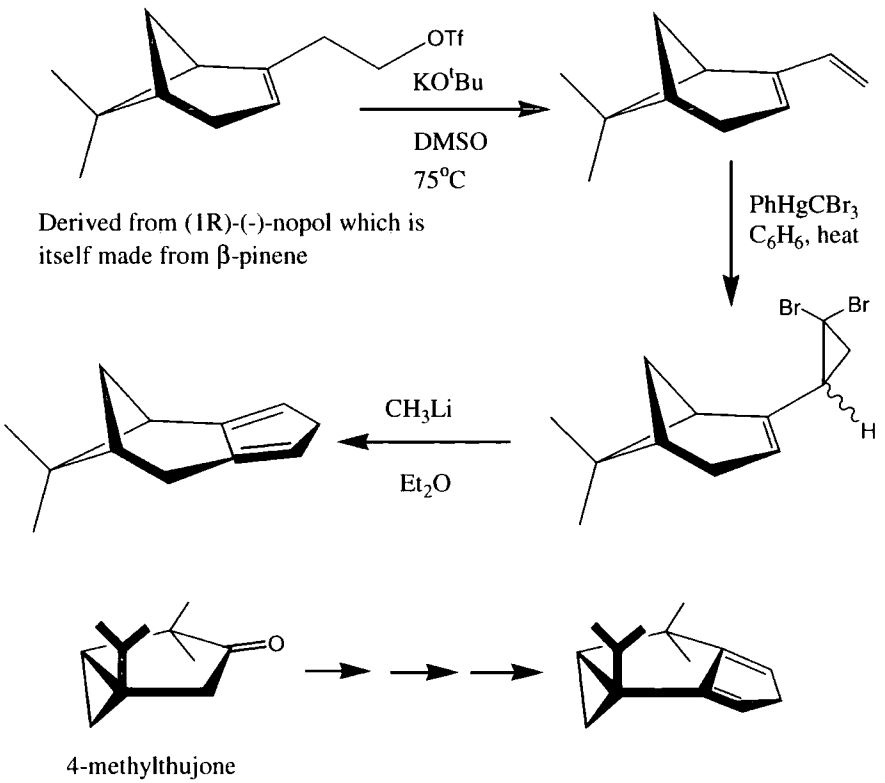


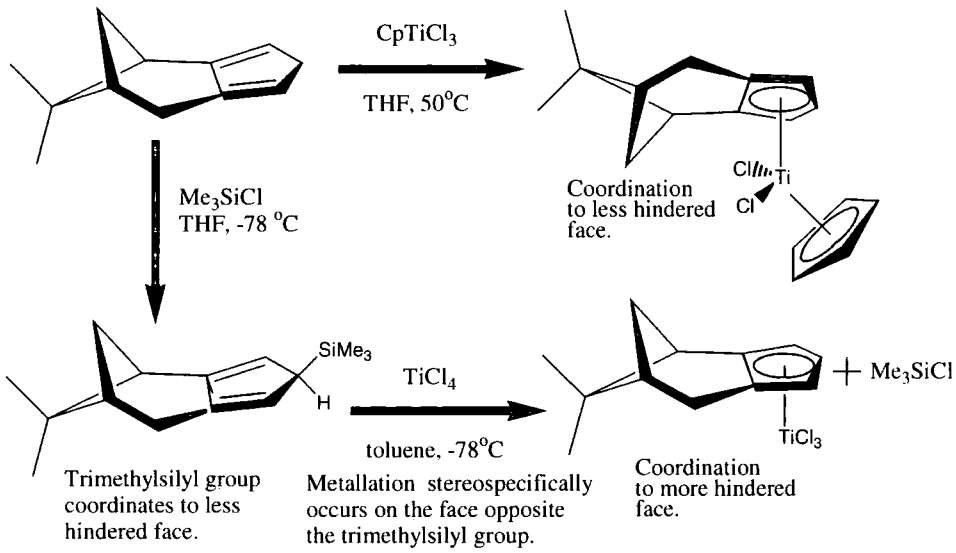
Figure 5. Formation of further C_1 symmetric annulated cyclopentadienes from terpenes[67, 68]



The two faces of terpene-derived annulated cyclopentadienyl ligands display different degrees of steric hindrance towards an approaching metal fragment and this normally leads to the preferential metallation of the least hindered face.[69] The diastereoselectivity of complex formation can be optimised by control of the reaction conditions[32] or it can be reversed by a silylation-metallation sequence (Figure 6).[69] The latter process has the added features of being clean, high yielding and only coordinating a maximum of one cyclopentadienyl ring to the metal.

Enantiotopically-faced prochiral cyclopentadienes are extremely easy to make but they give troublesome mixtures on metallation[71] (Figure 7), necessitating an enantiomeric resolution if an optically pure complex is to be prepared. Although a large number of examples of this class of ligand have been synthesised,[4] the present author has not seen any reference to their active investigation as catalysts, although bridged analogues, to be discussed later, have received a vast amount of attention.

Figure 6. Face selective metallation[69]



The above reactions have also been sucessfully been applied to the following two cyclopentadienes:

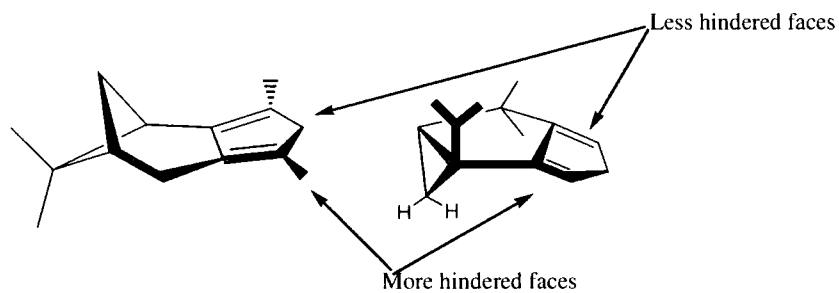
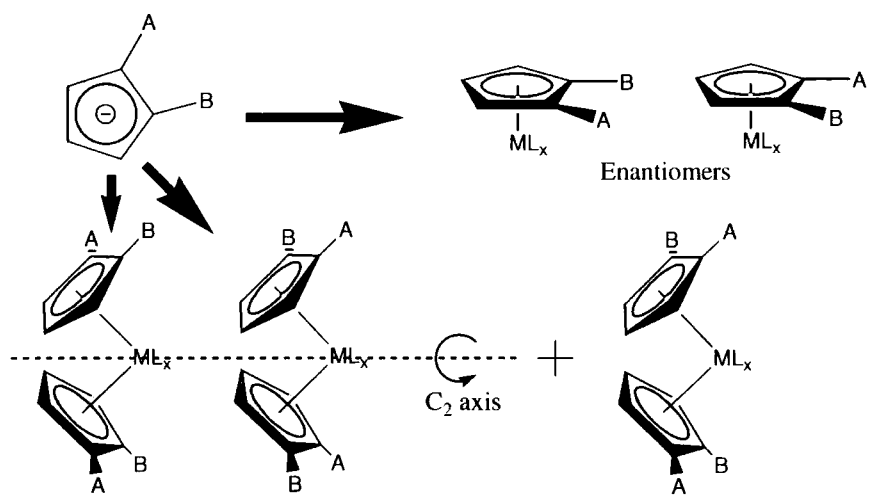


Figure 7. Metallation of enantiotopically-faced cyclopentadienes

In the following digrams, assume that all Cp rings are free to rotate. ML_x fragments are neither chiral or prochiral, for example, -FeCp or -$TiCl_2$

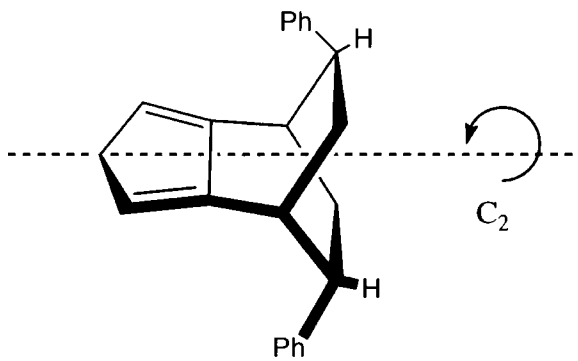


C_2 symmetric enantiomers, collectively termed the *rac* diastereomer.
(rac is derived from *racemic)*

Cs symmetric meso diastereomer. Achiral (although it may exist as two pseudoenantiomers given a suitable MLx fragment, e.g. -Ti(Cl)C_6H_5, see Figure 15)

Chiral annulated cyclopentadienes displaying C_2 symmetry have been much investigated on account of the convenient homotopicity of their faces. They have been synthesised in an enantiomerically enriched or enantiopure form either by the use of chiral starting materials, or chiral auxiliaries.[8]

Figure 8. A C_2-symmetric cyclopentadiene[37]



1.2.2 Survey of linked chiral and prochiral cyclopentadienes and some related compounds

1.2.2.1 Introduction to *ansa*-complexes

Metallocenes in which the two cyclopentadienyl rings are linked through any sort of bridging group are known as *ansa* compounds (Latin *ansa* = a handle (of a cup, jar or similar vessel), a loop[72]). These compounds display some important differences compared to the unbridged analogues – these differences will now be listed:

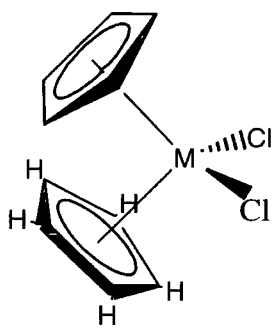
a) The chelate effect makes the bridged complexes even more stable than the unbridged compounds towards loss of cyclopentadienyl ligands, provided the bridging group is not so small as to produce excessive strain (c.f., decomposition of silyl-bridged ferrocenes[8]).

b) The bridge may alter the angle between the cyclopentadienyl rings either in the ground state complex or in a transition state, reactive intermediate or product and thus influence patterns of reactivity.[8, 33, 73, 74] An early example of this was the observation that the ethylene-bridged compound $[(CH_2)_2(\eta^5C_5H_4)_2]Fe$ could be protonated at iron much more easily than unsubstituted ferrocene under equilibrium conditions.[73] This thermodynamic effect was due to the ring-tilt and concomitant (Cp-centroid)-Fe-(Cp-centroid) angle strain which occurred on protonation of ferrocene already being present in the unprotonated bridged complex. A one atom bridge is particularly effective at opening up the opposite face of a complex, making the metal more reactive, electrophilic and accessible.[8]

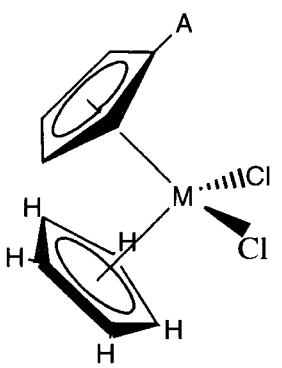
c) The cyclopentadienyl rings in an *ansa* complex cannot rotate around their respective axes. This has implications for NMR spectra since unsubstituted cyclopentadienyl ligands, or those substituted with small groups rotate sufficiently quickly as to render different magnetic environments invisible on a radio-frequency timescale (Figure 9). However, back-and-forth rotation or rocking through a small angle may still take place.[74]

Dissymmetric *ansa*-metallocene complexes can make very effective stereoselective catalysts due to the rigidity of the chiral environment around the metal. They receive particularly wide usage for olefin polymerisation.[2, 3]

Figure 9. Ring rotation and NMR in cyclopentadienyl complexes



Rapid rotation of the rings around the (Cp-centroid)-metal axes results in all the protons shown appearing to be in identical enviroments on the NMR timescale.



If the substituent 'A' is not sufficiently bulky to impede rotation of the unsubstituted ring then the protons shown will be equivalent on an NMR timescale.

1.2.2.2 Chirality in *ansa*-metallocenes: explanation of the classification system referred to in subsequent sections

For the purposes of the present work, bridged bis-cyclopentadienyl ligands are here classified into five classes. The classes are as follows:

I) Bridged bis(substituted cyclopentadienes) (achiral substituents) giving achiral dianions in which either Cp ring, taken separately, displays enantiotopic faces. Upon complexation of the first ring and concomittant production of a chiral group, the faces of the second ring become diastereotopic.

II) Bridged bis(substituted cyclopentadienes) (achiral substituents) in which the bridging unit is homochiral and the Cp rings have diastereotopic faces.

III) Bridged bis(substituted cyclopentadienes) (achiral substituents) in which the bridging unit is homochiral and the Cp rings have homotopic faces.

IV) Bridged bis(substituted cyclopentadienes) (achiral substituents) in which the bridging unit is achiral and one or both Cp rings have chiral substituents so as to give complexes with overall chirality.

V) Bridged bis(substituted cyclopentadienes) which will give chiral complexes but which do not fall in to one of the above categories.

1.2.2.2.1 Class I ligands and complexes thereof

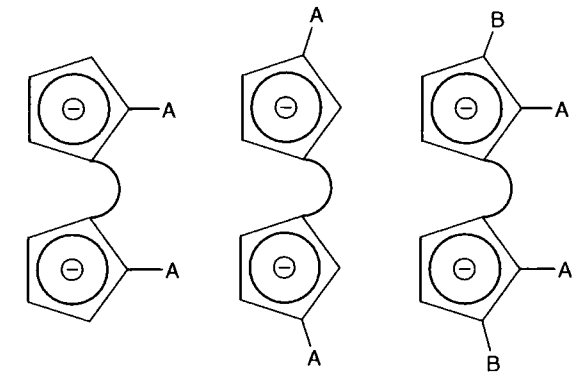
The simplest ligands capable of giving chiral *ansa*-metallocene complexes consist of two enantiotopically faced polysubstituted Cp groups linked as shown in Figure 10. Numerous variations on this theme are possible by varying the nature of the linking group and/or varying the number and position of the substituents R. Ligands of this type have the serious disadvantage of producing troublesome mixtures of *rac* and *meso* diastereomers on metallation, and even if the desirable *rac* form can be separated or selectively produced, it still has to be resolved if a homochiral complex is required.

The most intensively studied chiral *ansa*-metallocenes are those based on 1,2-bis(1*H*-inden-3-yl)ethane and 1,2-bis(4,5,6,7-tetrahydro-1*H*-inden-3-yl)ethane,[4] shown in Figure 11.

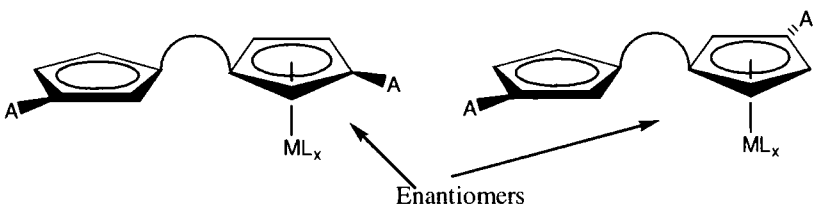
1,2-bis(1*H*-inden-3-yl)ethane is easily made by reacting lithium indenide with 1,2-dibromoethane.[75] Metal complexes are easily prepared by lithiating the bis(indenyl)ethane and reacting with metal chlorides, for example titanium tetrachloride,[76] zirconium tetrachloride[75] or lutetium or ytterbium trichlorides.[20] Improved yields were obtained by using very dilute reagent solutions.[77, 78 and references therein]

Figure 10. Linked enantiontopic bis(cyclopentadienyl) ligands

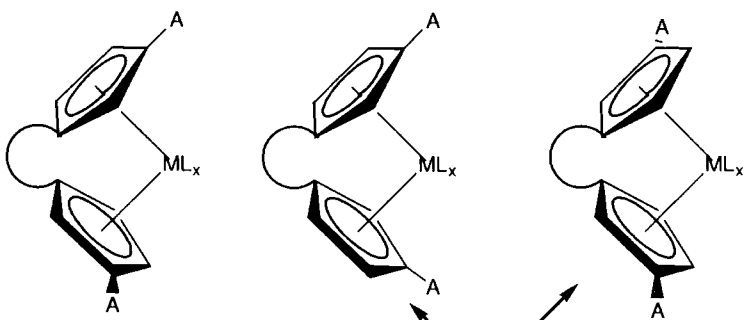
) = achiral bridging unit, e.g. $-CH_2CH_2-$ or $-SiMe_2-$.
A and B are achiral subsituents.



There are numerous variations on this theme .



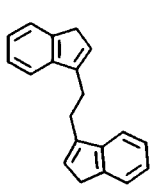
Either ring taken individually displays enantiotopic faces, but the chiral unit created by complexation of the first ring renders the second ring diastereotopic.



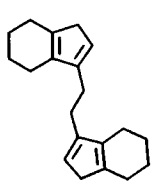
Achiral *meso* diastereomer

Enantiomers, collectively referred to as the *rac* diastereomer.

Figure 11. The $(EBI)H_2$ and $(EBTHI)H_2$ ligands



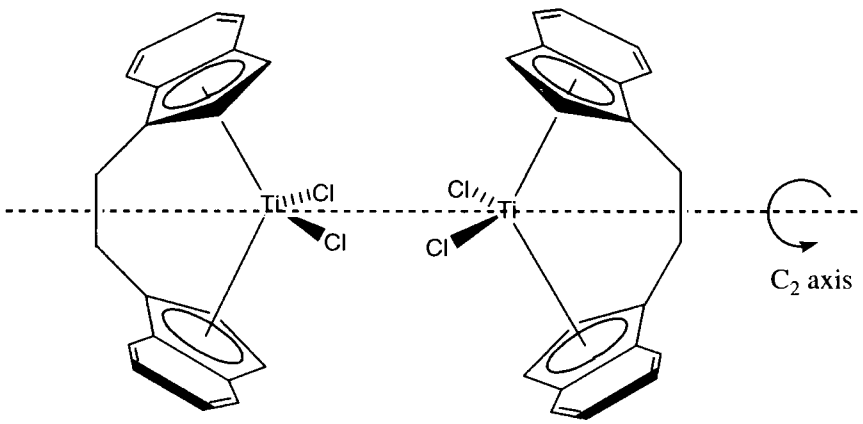
$(EBI)H_2$
1,2-bis(1*H*-inden-3-yl)ethane



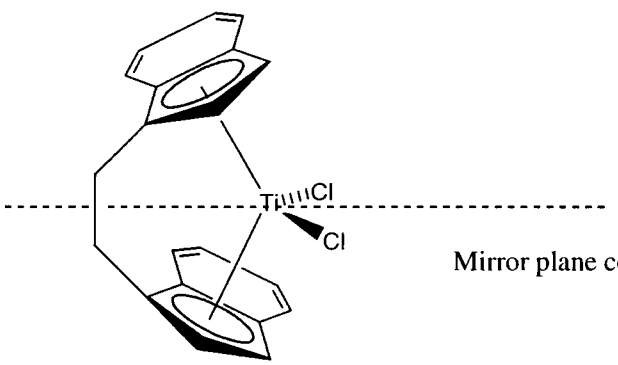
$(EBTHI)H_2$
1,2-bis(4,5,6,7-tetrahydro-1*H*-inden-3-yl)ethane

Taken individually, either cyclopentadienyl ring of the EBI dianion exhibits enantiotopic faces, but upon complexation of one ring to a metal and the concomitant generation of a chiral unit, the faces of the other Cp ring gain a diastereotopic relationship. Thus metallation gives two products as shown in Figure 12.

Figure 12 The stereoisomers of (EBI)$TiCl_2$



Enantiomers, collectively termed the *rac* diastereomer. C_2 symmetric.



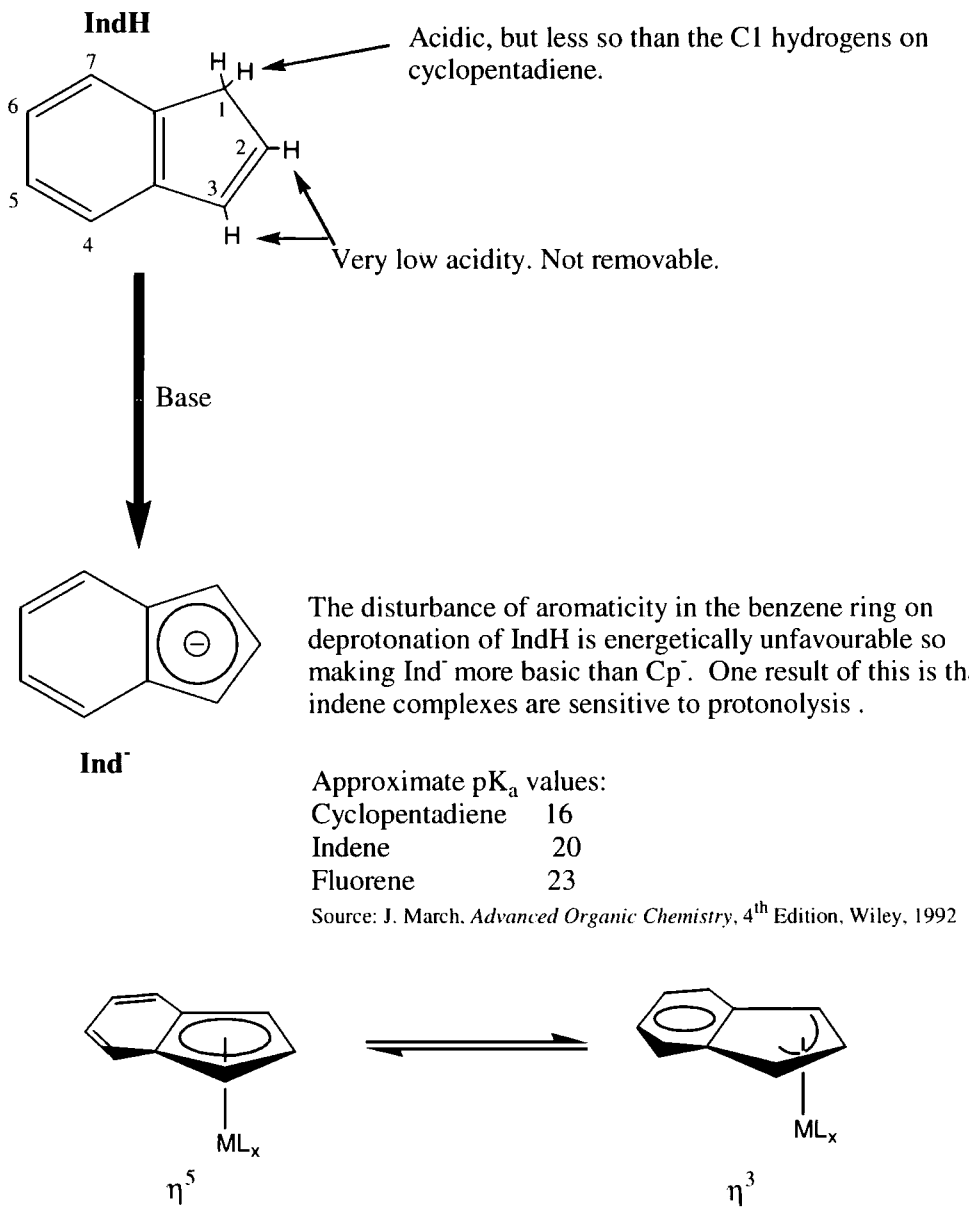
Mirror plane coplanar with Ti and both Cl.

Achiral *meso* diastereomer. C_s symmetry.

The reaction of lithiated cyclopentadienyl-based ligands with metal chlorides is predominantly kinetically controlled. In the case of class I *ansa*-ligands this results in the production of substantial amounts of *meso* isomer, despite the latter having greater intramolecular steric hindrance than the *rac* isomer. In the case of (EBI)$TiCl_2$, although it is produced in an initial *rac:meso* ratio of between 1:2 and 1:10, the *meso* form largely isomerises to the more stable *rac* under the influence of light.[76] It can be subsequently hydrogenated to non-labile (EBTHI)$TiCl_2$ and resolved by the use of a homochiral binapthyl ligand.[76]

The lability of indenyl complexes, particularly those which are unbridged and those which are bridged but strained, is due to the loss of aromaticity in the benzene ring which accompanies deprotonation and complexation (Figure 13). Indenyl complexes are often particularly sensitive to acids and water and chiral indenyl complexes may racemise in light. Tetrahydroindenyl complexes do not have these disadvantages. EBTHI complexes may be made by catalytic (PtO_2) hydrogenation of the corresponding EBI complex, at least for Ti and Zr. EBI and EBTHI complexes are important catalysts.[3, 17, 20, 75, 76]

Figure 13. Destruction of the aromaticity of the benzene ring in indene on deprotonation and complexation[79]



Besides EBI and EBTHI, many other class I ligands and complexes have been synthesised and their properties studied.[4, 6, 23, 47, 51, 53, 80 - 84] The aim behind much (although not all*) of this research has been both to create ligands which give only the *rac* diastereomer on metallation and to produce complexes with improved catalytic properties.

The principle methods of increasing the *rac*:*meso* ratio (and increasing the yield) in the metallation of *ansa*-cyclopentadienyl ligands (besides using a chiral bridging group – see the next section) are as follows: (Reference should also be made to Table 1 and to the associated diagrams (Figure 14).

A) Incorporation of bulky groups in such positions as to make the *meso* diastereomer excessively hindered. [Refs. 3d – f in ref. 79] As an example, compare the entries for ligands l, m, n, o, p and q in Table 1. Ligand l has methyl groups placed so as to cause only minor steric effects and metallation gives an essentially statistical 1:1 *rac*:*meso* mixture. Incorporation of bulky substituents nearer the bridging group, as in m, n, o and q, gives a ratio in favour of the *rac* complex on metallation.† If the ligand were metallated under thermodynamically controlled conditions, the ratio might be even more favourable (see below).

B) Varying the nature and/or position of the bridging group. Although changing between dimethylene, dimethylsildiyl, *N*-methylpiperidin-4,4-diyl or phen-1,2-diyl bridges causes appreciable variations in the geometry and reactivity of complexes, rather unsurprisingly none of them have a large influence on *rac-meso* selectivity. However, if sections of the bridge are incorporated into rings fused to the Cp groups, as in ligand r, steric hindrance in the *meso* isomer may be so large that it will not form. A trimethylene or longer bridge gives selectivity for the *rac* isomer in bis(indenyl) or bis(tetrahydroindenyl) complexes, but gives complexes with poor stereochemical definition.[79 and refs. therein]

C) Changing the conditions or nature of the metallation reaction. The product ratio of the reaction between a lithiated *ansa* metallocene and a metal chloride is largely determined by the reaction kinetics. This usually results in a sub-equilibrium yield of the *rac* form, although sometimes subsequent processes, e.g., heating in a donor solvent (for Y or Sc metallocenes[54] or lanthanidocenes) or photolysis can be used to cause isomerisation to a *rac-meso* mixture of thermodynamically determined proportions.[76, also see refs. in 81] There is the

---

* The main rationale behind some of the research was to produce complexes with improved conformational rigidity or to study the effect of varying the spacing and bite-angle between the chelating Cp rings.[80, 82]

† If the substituents are excessively bulky, as with the $SiMe_3$ groups in ligand p, then a metallocene may not form at all.

problem, however, that complexes which can interconvert between isomers in this way will racemise easily. Heating a bridged bis-cyclopentadiene with a metal amide in an unreactive solvent (typically toluene or a higher boiling analogue) results in amine elimination and formation of a metallocene amide complex.*, [78, 85, 86] Elimination reactions of this type are largely controlled by thermodynamics and for those ligands which are thermally stable and give complexes for which the *rac* and *meso* isomers have appreciably different free energies of formation, this method of complexation can give good diastereoselectivity for the *rac* form.[see refs. in 81] This is illustrated, for example, by entries 9 and 10 in Table 1. In favourable systems, amine elimination reactions can give much higher yields than the metal chloride + lithiated ligand method of synthesising *ansa*-metallocenes.[78] However, amine elimination is less effective with hafnium or titanium based systems than with zirconium and it gives poor results if there is steric hindrance in either the amide† or cyclopentadiene, or if the latter is insufficiently acidic.[78, 87] To extend the usefulness of the amine elimination method, work was done on the use of bis(alkyl)aluminum derivatives of *ansa*-cyclopentadienes as a ligand source rather than the cyclopentadienes themselves.[87] It was found that the compounds formed by reacting lithiated *ansa*-cyclopentadienes with $AlMe_2Cl$ would readily react with tetra(dimethylamido)-zirconium and -hafnium to give the metallocene amide plus $Al_2Me_4(\mu\text{-}NMe_2)_2$. The reaction proceeded under relatively mild conditions and was thermodynamically controlled. Silylamine elimination from $Ln[N(SiHMe_2)_2]_3$ (but not the excessively hindered $Ln[N(SiMe_3)_2]_3$) has been used as a highly effective way of synthesising *ansa*-lanthanidocenes and the reactions involved have recently been studied in detail.[6]

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* Metallocene amides can be converted to the corresponding metallocene chloride by the action of dimethylammonium chloride[82] or trimethylsilyl chloride. [78]

† As an example of the influence of bulky groups, consider the difference in reactivity between $Zr(NMe_2)_4$ and $Zr(NEt_2)_4$. The former amide reacts with $(EBI)H_2$ in toluene (100 °C, 17 h) to give a very high yield of $(EBI)Zr(NMe_2)_2$ while the ethyl analogue only attacks one indenyl group under the same conditions to give $(\eta^5\text{-}C_9H_6CH_2CH_2C_9H_7)Zr(NEt_2)_3$. Tetrakis(diethylamido)zirconium does react with both rings if heated in 1,2-dichlorobenzene at 180 °C, but under these conditions gives $(EBI)ZrCl_2$, and with very poor diastereoselectivity. [78]

Table 1. Metallation of cyclopentadienes

Entry number	Ligand (See Figure 14)	Metal	Metallation method*	*Rac:meso* molar ratio†	Overall yield of mixture‡ /%	Reference
1	a	Ti	i	1:2-10	22	76
2	a	Yb	i	-	54	20
3	a	Lu	i	3:1	30	20
4	a	Zr	i	§	(66)	75
5	b	Zr	i	5:1	22	51
6	c	Ti	ii	4:1	89	6
7	c	Zr	i	3:2**	-	6
8	d	Ti	ii	1:1	89	82
9	d	Zr	i	3:2	83	82
10	d	Zr	iii	10:1	(67)	82
11	e	Zr	iii	8:1	(59)	82
12	f	Ti	ii	4:1	77	82
13	f	Zr	i	10:1	(61)	82
14	f	Zr	iii	10:1	(61)	82
15	g	Ti	ii	1:1	92	82
16	g	Zr	i	10:1	(74)	82
17	h	Ti	ii	1.1:1	53	23
18	i	Ti	ii	3.6:1	64	23
19	j	Zr	i	1:1	42	83
20	k	Y	iv	3:1	95	53(Also see 6)
21	l	Ti	v	~1:1	36	84
22	m	Ti	v	4:1	88	84
23	n	Ti	v	2:1	76	84
24	o	Ti	v	3.6:1	74	84
25	p	Ti	v	No metallocene	-	84
26	q	Ti	v	4.3:1	-	84
27	r	Zr	i	Rac only	30	81

* Metallation methods: (see original papers for solvents &c)

i) Lithiated ligand + metal chloride ($TiCl_4$, $ZrCl_4$, YCl_3, $LnCl_3$).

ii) Lihiated ligand + $TiCl_3$ followed oxidation with air and/or HCl.

iii) Neutral ligand + $Zr(NMe_2)_4$, heat.

iv) Neutral ligand + $Y[N(SiHMe_2)_2]_3(THF)_2$, heat (Eliminate $HN(SiHMe_2)_2$). Convert resulting yttrocene silylamide to the corresponding chloride by treatment with dimethylammonium chloride.

v) Lithiated ligand + TiCl3 followed by oxidation (HCl + air) and catalytic hydrogenation (H_2, PtO_2) to give tetrahydroindenyl analogue.

† *Rac:meso* ratio can be rather sensitive to the reaction conditions since the conditions determine the extent to which kinetics and thermodynamics influence the outcome.

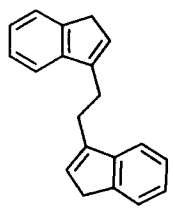
‡ The values in brackets refer to the yield of *rac* isomer after separation from the *meso* product.

§ The *rac;meso* ratio of the initial product was not given but was probably high since a simple crystalisation gave a 66% yield of >97% pure *rac* complex.

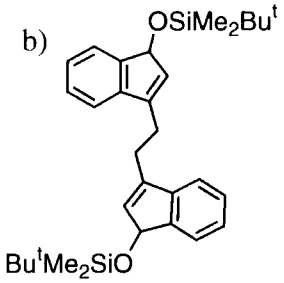
** Photoisomerises to a 93:7 *rac:meso* mixture.

Figure 14. Figure to accompany Table 1, showing the structures of the ligands in the table.

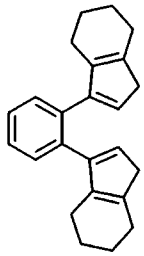
a)



b)



c)



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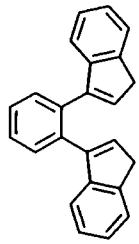

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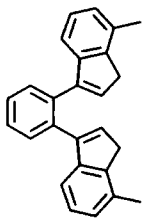

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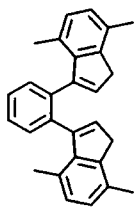

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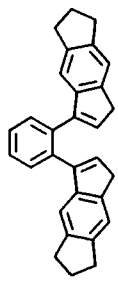

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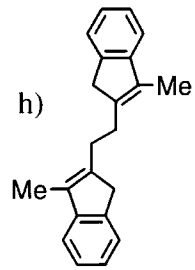

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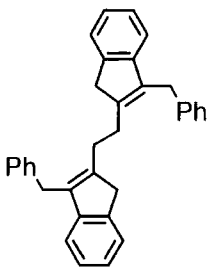

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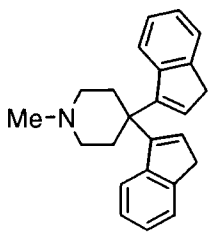

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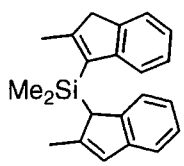

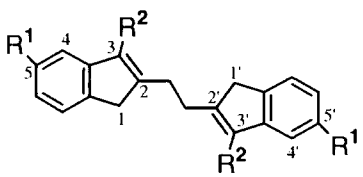

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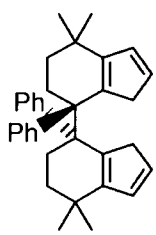


	R^1 =	R^2=
l	Me	H
m	H	^{i}Bu
n	H	^{i}Pr
o	H	CH_2Ph
p	H	$SiMe_3$
q	H	Ph

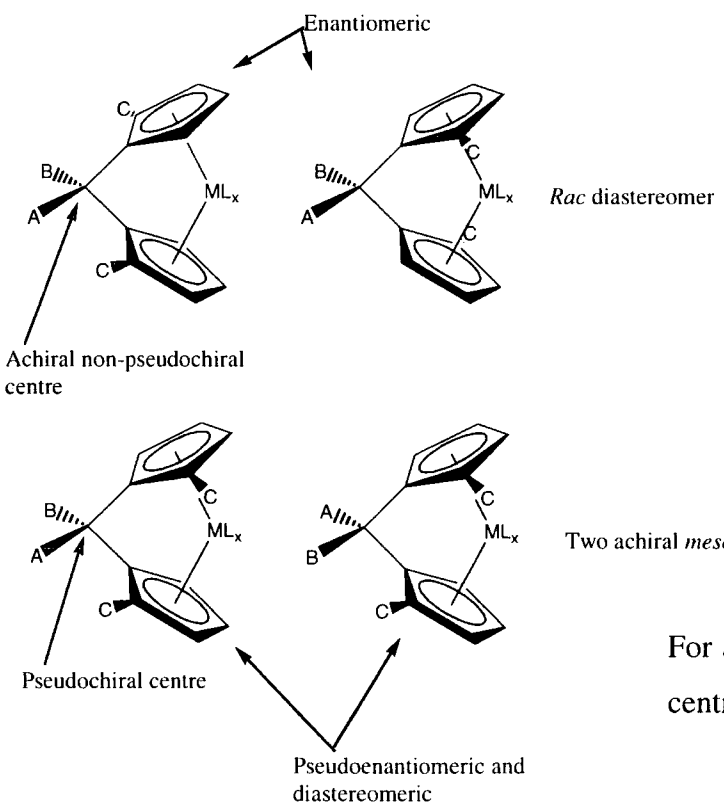
1.2.2.2.2 Bis-cyclopentadienes containing a chiral bridging group (class II ligands) and complexes thereof

There is currently considerable interest in synthesising linked cyclopentadienes in which the linking unit is chiral and enantiomerically pure. The advantage of this type of ligand is that metallation is more or less enantio- and diastereo-selective thus reducing or eliminating the need for purification or resolution of the complex. Resolution may still be required as a step in ligand preparation[79, 88] since homochiral starting materials[48, 89] or enantiospecific reactions directed by chiral auxiliaries are not applicable to all systems. However, resolution of an air and water stable organic compound, usually by salt or ester formation using a cheap homochiral acid or base, is technically much easier than resolution of a sensitive and often not very soluble metal complex. There is also the advantage that a large bulk of enantiopure organic compound may be prepared and used to make numerous batches of various metal complexes.

The various diastereomers formed by *ansa*-metallocenes incorporating a chiral bridge are shown in Figure 15, Figure 16 and Figure 17.

Some prominent examples of class II ligands and some complexes derived therefrom are shown in Figure 18.

Figure 15. Examples of stereoisomerism of *ansa*-metallocenes incorporating a chiral or pseudochiral bridge



A, B. C and L are achiral groups

For a related situation in which the metal is a centre of pseudochirality, see ref.66.

Figure 15 continues as Figure 16 on the next page

Figure 16. Stereoisomerism of *ansa*-metallocenes incorporating a chiral or pseudochiral bridge, continued from Figure 15

A, B, C, D and L are achiral groups

This symbol indicates pairs of enantiomers

This arrow indicates a diastereomeric relationship

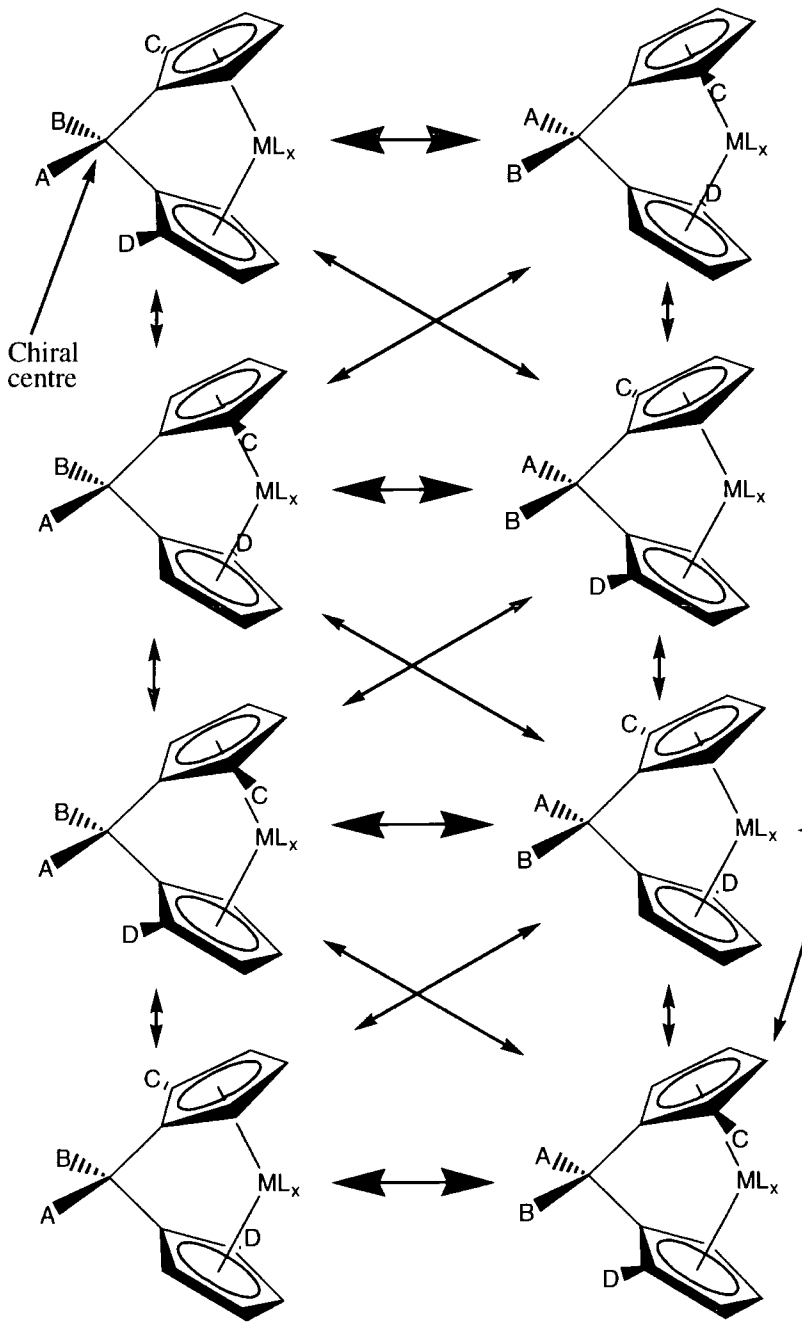
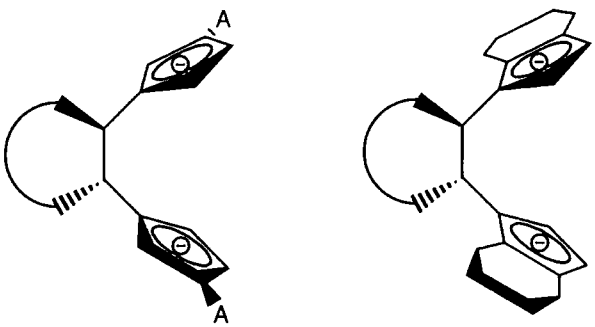


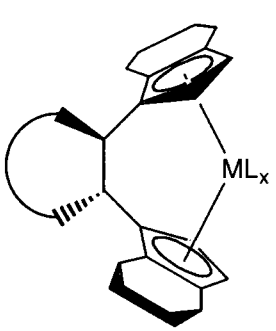
Figure 16 continues as figure 17 on the next page

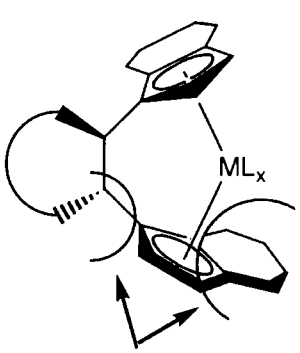
Figure 17. Stereoisomerism of *ansa*-metallocenes incorporating a chiral or pseudochiral bridge, continued from Figure 16

Class II ligands

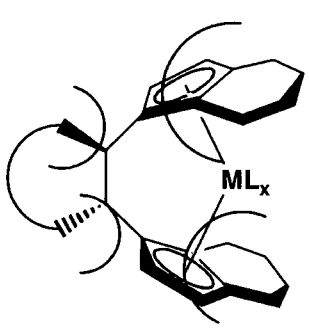


These can give single enantiomeric forms of up to three diastereomers on metallation, but for many systems, the two hindered isomers are too energetically unfavourable to be produced.



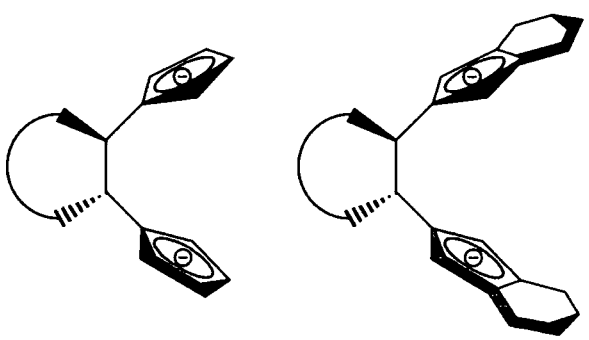


Steric hindrance



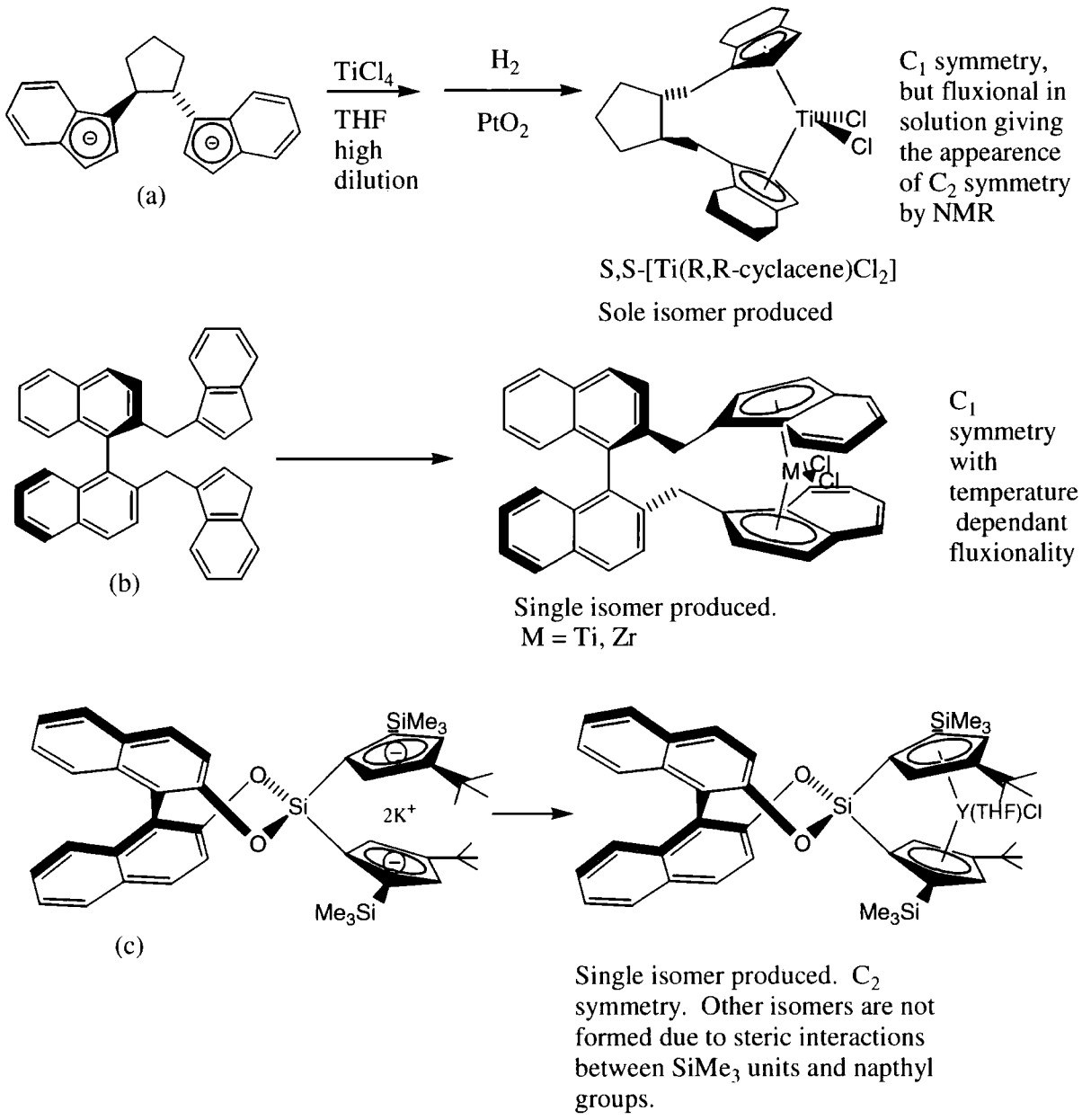
Severe steric hindrance

Class III ligands



These give only one enantiomer of a single diastereomer on metallation.

Figure 18. Some prominent examples of class II ligands and complexes thereof



Refs: (a) 89, (b) 90, (c) 5.

One problem with metallation reactions involving class II bridged cyclopentadienes is that reaction of the metal with the first Cp ring may not be diastereospecific for the 'correct' face. If this is so, then those metal fragments which bond to the 'wrong' face, will either give rise to an undesirable stereoisomeric impurity[48] or in stereochemically demanding systems, will be geometrically unable to bond to the second Cp ring of the same molecule. In the latter case, the 'wrongly' positioned metal fragments attack other ligand molecules, giving rise to oligomers.[89, 90] Oligomer formation results in low yields (typically 20%) but does not usually cause a separation problem. Ligands (a) and (b) (Figure 18, previous page) suffer from oligomer formation on metallation but (c) gives the complex shown in 75% yield when reacted with YCl_3-THF adduct. It is thought that in the latter case, there may be favourable diastereoselectivity during complexation of the first ring.[5]

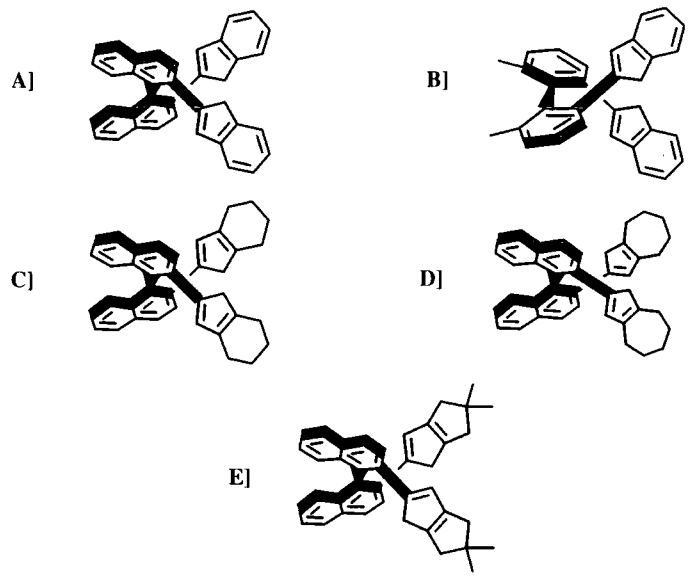
For further information on class II ligands and their complexes, refer to refs. 5, 48, 79, 88 - 90.

1.2.2.2.3 Class III ligands and complexes thereof

Class III ligands* have been synthesised to avoid the problems mentioned in the previous paragraph. Prominent examples are shown in Figure 19 (next page). Ligand **A** was found to be largely useless on account of an inability to form stable complexes.[79, 88] Ligand **B** formed acid sensitive complexes with Ti and Zr which were not isolated but immediately hydrogenated to the much more robust bis(4,5,6,7-tetrahydroinden-2yl) analogues. The acid sensitivity of the 2-indenyl complexes was investigated.[79] Lithiated **E** did not metallate on reaction with Ti or Zr chlorides; the reason for this was not apparent, but may have been due to possible complexes being excessively strained. However, C_2 symmetric complexes were easily prepared from **C** and **D**.[88]

* See Figure 17 for an illustration of the difference between class II and class III ligands.

Figure 19. Some prominent class III ligands (chiral bridge, homotopic Cp faces)



Refs: **A]** & **B]** 79, **A]**, **C]**, **D]**, & **E]** 88.

1.2.2.2.4 Other types of ansa-*metallocene.*

Chiral *ansa*-cyclopentadienyl complexes employing an achiral bridge but having a chiral group bonded to one or both rings (i.e., based on class IV ligands) have been synthesised and studied[18, 26, 42] but the general principles they involve have already been discussed. As these complexes are not particularly notable, and due to considerations of space, they will not be discussed further.

An interesting type of chiral *ansa* cyclopentadienyl complex has recently been described.[91] As shown in Figure 20, this new type of ligand is axially chiral* on account of hindered rotation of the fluorenyl group about the fluorenyl-napthyl bond. The ligand can be synthesised enantiospecifically, produces a homochiral complex on metallation and has been produced as an outgrowth of research into structurally related bridged indenyl-(aryl/alkyl)oxide ligands.[92, 93]

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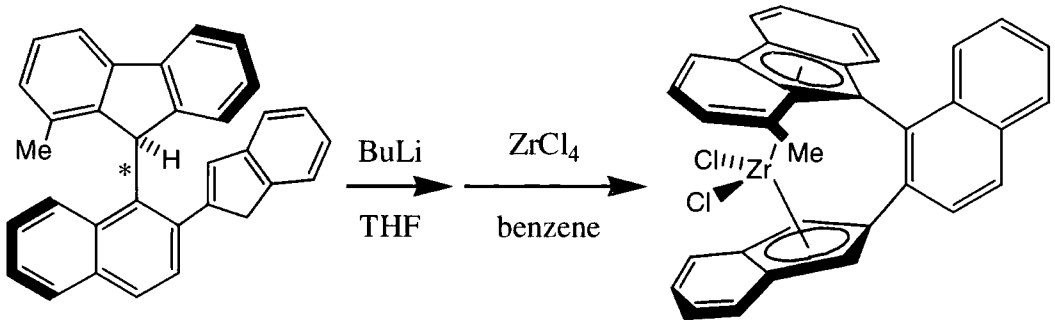
* Note: The ligand is both axially chiral and possesses a chiral carbon atom (the fluorenyl carbon attached to the starred bond in Figure 20). Thus, either inversion around the chiral atom, or a 180° rotation of the fluorenyl group relative to the rest of the molecule would, done singly, result in the formation of a new diastereomer. Both operations would have to be completed to interchange the enantiomers. In the deprotonated ligand, there is no distinct chiral centre but the axial chirality remains and serves to direct the stereochemistry of metallation.
In the complex, there are no discrete chiral centres and there is no distinguishable axial chirality. The fluorenyl Cp ring has diastereotopic faces of the usual type and the chirality of the complex is a consequence of its overall C_1 symmetry. The fact that the complex is chiral is quite unrelated to the presence (or otherwise) of hindered rotation and consequent axial chirality in the free ligand. The stereochemical features of the free ligand and of the complex must not be confused; the complex is not axially chiral and has chirality no different from any other bis-Cp complexes, linked or not, in which there are no chiral substituents, one ring has homotopic faces and is non-prochiral and the other ring has enantiotopic faces and is prochiral (see Figure 2a for an illustration of the latter type of ring). The novelty lies in the enantiocontrol exerted by the hindered rotation during the metallation of the ligand.

Figure 20. A recently synthesised axially chiral *ansa*-ligand[91]



Axially chiral due to hindered rotation around the starred bond.

C_1 symmetry

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2 Synthesis of substituted cyclopentadienes

2.1 General introduction: scope of the chapter

A substantial proportion of the experimental part of this thesis involved synthesising novel cyclopentadienes. As such, it is highly relevant to include a chapter reviewing some of the techniques available to the organometallic chemist wishing to synthesise cyclopentadienyl ligands. A further consideration in the writing of this chapter was a desire to provide an introductory text for the benefit of subsequent workers carrying on cyclopentadienyl chemistry. The chemical literature pertaining to the synthesis of cyclopentadienes and cyclopentadiene precursors, particularly cyclopentenones, is gigantic and of such scope that it cannot be dealt with comprehensively in this work. Instead of providing a wide-ranging but non-detailed review, a limited number of synthetic methods have been picked out and described in some depth. The criteria for selection will now be outlined:

a) The syntheses should be of interest to the organometallic chemist. This might sound like an obvious point, but not all syntheses which may be of use to the synthetic organic chemist are useful for the production of cyclopentadienyl ligands. Many syntheses employed by organic chemists, for example for the production of cyclopentenone prostaglandins, are excellent for the synthesis of complex and precise multifunctional molecules, but are unnecessarily expensive, complicated and too restricted in scale for the manufacture of batches of cyclopentadienyl ligands. Not all of the reactions dealt with in this chapter have actually been applied to the synthesis of ligands, but they all have potential to be thus employed.
b) Synthetic methods relevant to the synthetic part of the thesis have been given particularly good coverage.
c) Cyclopentenones are very useful and practical precursors to all manner of useful cyclopentadienes. Cyclopentenones are also important in natural-product chemistry and thus their synthesis has been well investigated. An early decision was therefore made to pay particular attention to discussing cyclopentenone synthesis and the conversion of cyclopentenones to cyclopentadienes.

Within the cyclopentenone section, the base induced cyclisation of 1,4-diketones has been dealt with at some length. This is because it forms a good introduction to the synthesis of cyclopentenones as it involves conceptually simple classical carbonyl chemistry as well as being a practical route to cyclopentenones.

2.2 The cyclopentenone route

2.2.1 Introduction: the importance of cyclopentenones

Cyclopentenone and cyclopentenone derivatives are useful starting materials for the preparation of substituted cyclopentadienes. Cyclopent-2-en-1-one and its derivatives are more common than the 3-en-1-one isomers (Figure 1), indeed cyclopent-2-en-1-one itself is a commercial product, although rather expensive.* Nucleophilic addition to the ketone moiety, followed by dehydration of the resulting alcohol, normally facile on account of the conjugated double bond, is a straightforward method of generating various substituted cyclopentadienes.

Figure 1. The two isomers of cyclopentenone

cyclopent-2-en-1-one cyclopent-3-en-1-one

Due to the effects of conjugation, cyclopent-2-en-1-one is the more thermodynamically stable isomer.

Many natural products are substituted cyclopentenones, and numerous synthetic examples are of interest on account of their biological effects.[1, 2, 3] For example, the compound shown in Figure 2 is an experimental anti-fungal agent while a wide range of cyclopentenones, of the general formulae shown in Figure 3, were synthesised by the Pauson-Khand reaction and found to be biochemically active in plants. Of particularly enormous importance in this context are the prostaglandins, a group of compounds of profound biochemical importance to the human body. Jasmone (Figure 4), a compound derived from oil of jasmine, is another substituted cyclopentenone and of importance as a result of its long use in perfumery. Figure 5 shows an experimental cyclopentenone-based drug. Aflatoxins, infamously toxic and carcinogenic fungal metabolites, contain an annellated cyclopentenone unit.[4] Thus, organic chemists have long been stimulated to investigate cyclopentenone syntheses, and this is of great advantage to the organometallic chemist wishing to utilise cyclopentenones as a precursor to cyclopentadienes.

Figure 2. An experimental cyclopentenone antifungal agent[3]

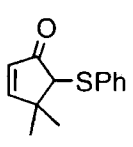
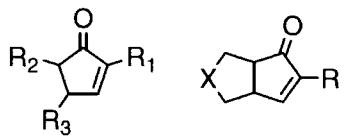


Figure 3. Cyclopentenones with plant growth regulating properties[2]



Cyclopentenones with these general formulae and with a wide range of substituents R_n and X possess biochemical activity in plants.

Figure 4. *Cis*-Jasmone, a botanical cyclopentenone

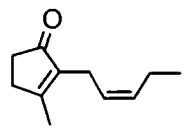
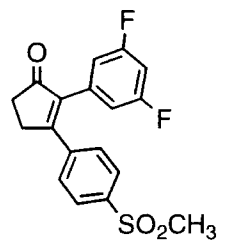


Figure 5. An experimental non-steroidal anti-inflammatory cox-2 enzyme inhibiting drug based around a cyclopentenone ring[1]



Early reviews of pioneering prostaglandin syntheses are available.[5, 6] For references to early methods of synthesising 2-substituted cyclopent-2-en-1-ones, see the paper by Ansell and Ducker.[§]

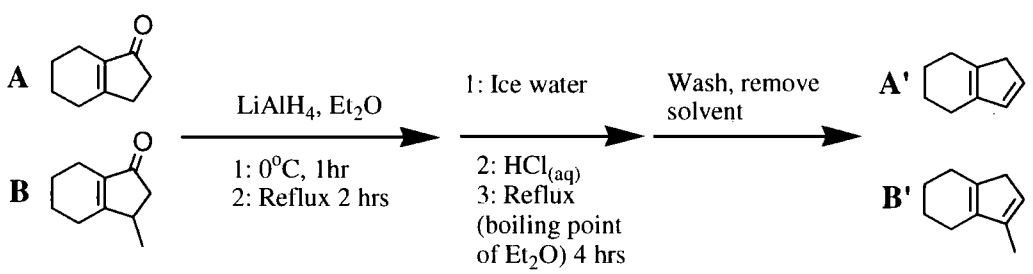
* Aldrich 2003-2004 £64.50/25g

2.2.2 The synthesis of cyclopentadienes from cyclopentenones

2.2.2.1 Use of nucleophilic reagents including complex hydrides, Grignard reagents and lithiated organyls

Converting cyclopentenones into cyclopentadienes is a straightforward process. The simplest procedure, used when no further substituents are to be incorporated, is to reduce the ketone to an alcohol using a complex hydride reducing agent. The alcohol is then dehydrated, this step usually being unproblematic as the new double bond is conjugated and at least disubstituted. Indeed, dehydration often occurs spontaneously during work-up with dilute aqueous acid. Figure 6 shows an example from the work of Nile and co-workers.[7] The cyclohexannulated cyclopentenones were prepared from cyclohexene and either acrylic or crotonic acid by an aliphatic Friedel-Crafts Nazarov procedure, a method discussed at length later in this chapter.

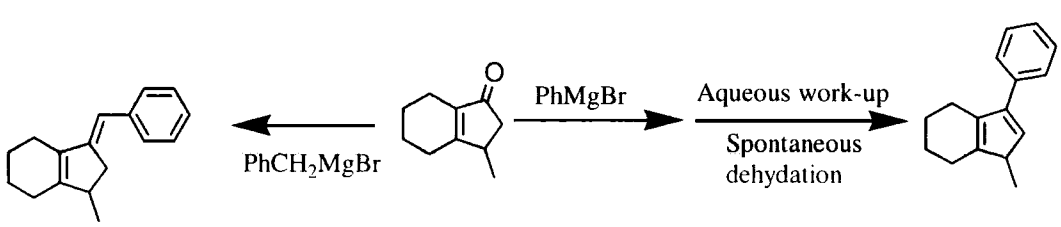
Figure 6. Preparation of a cyclopentadiene by reduction of a cyclopentenone (ref. 7)



(A' and B' were produced as mixtures of isomers. B' could be vacuum distilled, although the isomers were not separated. A' polymerised quickly and was used crude, although a small sample was successfully purified by chromatography.)

By using a suitable nucleophilic reagent, instead of a complex hydride reducing agent, substituents can be introduced as part of the cyclopentadiene synthesis. For example, cyclopentadienes have been made by reacting cyclopentenones with Grignard reagents,[7 - 10] lithium alkyls,[10] lithiated imines[11] and lithiated acetonitrile.[11] Figure 7 shows two examples from work done previously at Durham.[8, 10]

Figure 7. Cyclopentadienes from cyclopentenones plus Grignard reagents

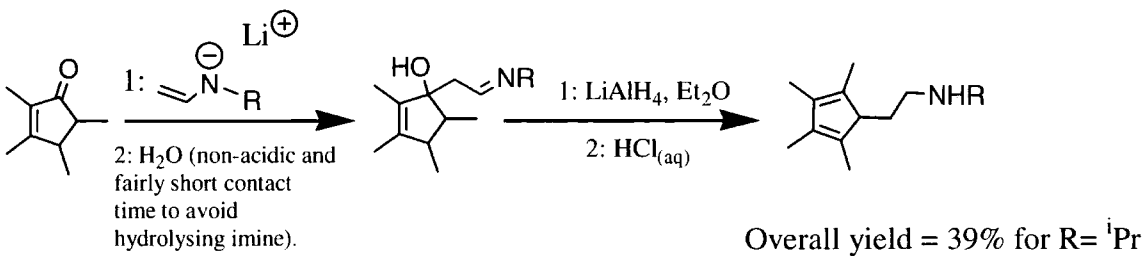


As can be seen from Figure 7, problems can arise in the form of exo-cyclic double bond formation, if an unsaturated group capable of conjugating with a exo-cyclic, but not an *endo*-cyclic, double bond is attached. However, if further synthetic steps result in the saturation of the formerly unsaturated group then a treatment with acid will result in an exo- to endo- double bond isomerisation. For example, reaction of 2,3,4,5-tetramethylcyclopent-2-en-1-one with allylmagnesium bromide gave a mixture of $(C_5Me_4)CH_2CH{=}CH_2$ and the exo-cyclic double bond isomer, $(C_5H_2Me_4){=}CHCH{=}CH_2$.[9] The corresponding terminal alcohols were produced by hydroboration of the mixture, using 9-BBN or disiamylborane. The mixture of alcohols, $(C_5Me_4)CH_2CH_2CH_2OH$ + $(C_5H_2Me_4){=}CHCH_2CH_2OH$, was tosylated with *p*-$MeC_6H_4SO_3Cl$ in pyridine and during the acidic work-up, an isomerisation occurred resulting in a product containing no detectable amount of the undesirable exo-cyclic double bond isomer. For a further example of this type of process, see ref. 11.

1-Benzyl-2,3,4,5-tetramethylcyclopentadiene was produced as *endo*-cyclic double bond isomers by a dehydration in refluxing acidic benzene.[12] The clear implication is that the *endo*-cyclic double bond isomers are the thermodynamically preferred products, probably as a result of the energetic favourability of having both double bonds tetra-substituted. The contrast with the example of benzyl substitution on the previous page (Figure 7) should be noted.[8, 10]

The reaction of lithiated imines with cyclopentenones is useful and important as it affords a practical method of synthesising cyclopentadienyl ligands which can chelate through a pendant CH_2CH_2NHR unit (Figure 8).[*, 11] The use of lithiated acetonitrile is also a route to these compounds as the CN unit is readily reduced to CH_2NH_2, which can then be substituted at nitrogen. Acetonitrile must be used if an NHMe group is required as *N*-methyl imines are unstable and difficult to handle.[11]

Figure 8. Reaction of a cyclopentenone with a lithiated imine



R= ^{t}Bu, ^{i}Pr.

For R= ^{t}Bu, the alkylation and reduction was done as a one-pot process of 21% yield.

* For a general method of alkylating imines (but with 2-methoxyallyl bromide as the electrophile) see ref. 15, bottom of p2547. Also see G. Stork and J. Benaim, *J. Am. Chem. Soc.*, **93**, 5938, (1971) for further information on imine alkylations.

2.2.2.2 Alkylation of cyclopentenone enolates

If a cyclopentenone is to be converted into a more highly substituted cyclopentadiene than a simple Grignard reaction will achieve, then the cyclopentenone may be deprotonated with LDA and the resulting enolate subsequently alkylated with an alkyl bromide, or other electrophile. This gives a substituted cyclopentenone, which may be further substituted by the same method if required. The final conversion to a cyclopentadiene is then carried out by means of either a complex-hydride reduction or a Grignard reaction as already discussed.

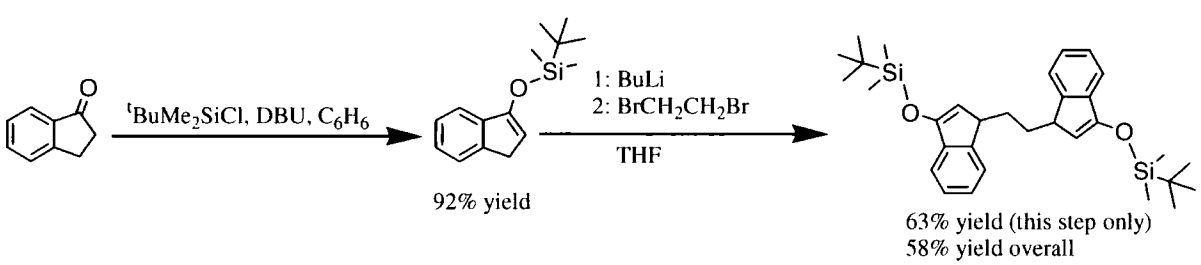
Mintz and co-workers alkylated the enolate of 2,3,4,5-tetramethylcyclopent-2-en-1-one to give 2-alkyl-2,3,4,5-tetramethylcyclopent-2-en-1-one.[12] $LiAlH_4$ reduction gave the alcohol, 2-alkyl-2,3,4,5-tetramethylcyclopent-2-en-1-ol. This was dehydrated in hot benzene using acid catalysis. Importantly, dehydration was accompanied by a 1,2-alkyl shift resulting in the production of a useful 1-alkyl-2,3,4,5-tetramethylcyclopentadiene.

2.2.2.3 *O*-Silylation as a method of producing cyclopentadienyl ligands from cyclopentenones

Indan-1-one, the indenyl analogue of cyclopent-2-en-1-one, has been converted to siloxy-substituted indenyl ligands by the simple process of reaction with a trialkylsilyl chloride in the presence of a non-nucleophilic base. Silyl enol ether formation is an efficient, high yield process, but siloxy substituents do not have such a desirable level of inertness in the final complex as do hydrocarbyl groups.

A reasonably recent example of the use of *O*-silylation in the preparation of cyclopentadienyl (more specifically, indenyl) ligands is given by Leino;[13] the synthesis is outlined in Figure 9.

Figure 9. Preparation of an indenyl ligand by *O*-silylation of indan-1-one



2.2.3 The synthesis of cyclopentenones from 1,4-dicarbonyl compounds

2.2.3.1 Introduction: cyclisation of 1,4-diketones under acidic and basic conditions

A 1,4-dicarbonyl compound with an acidic hydrogen delta to a suitably electrophilic carbonyl will undergo an intramolecular aldol reaction in basic solution, see Figure 10. The initially produced hydroxycyclopentanone either spontaneously dehydrates during the work-up, or is subjected to a mild dehydration step to give the required cyclopentenone as the most stable double-bond isomer. This is a classic and still useful route to cyclopent-2-en-1-ones, and the method is versatile as there are a large number of methods of synthesising the required 1,4-dicarbonyl compounds.[14, 15, 17]

1,4-diketones can cyclise under acidic conditions (Figure 11), but this reaction produces furans rather than cyclopentenones. The two modes of cyclisation must not be confused.

Figure 10. Cyclisation of 1,4-diketones under basic conditions

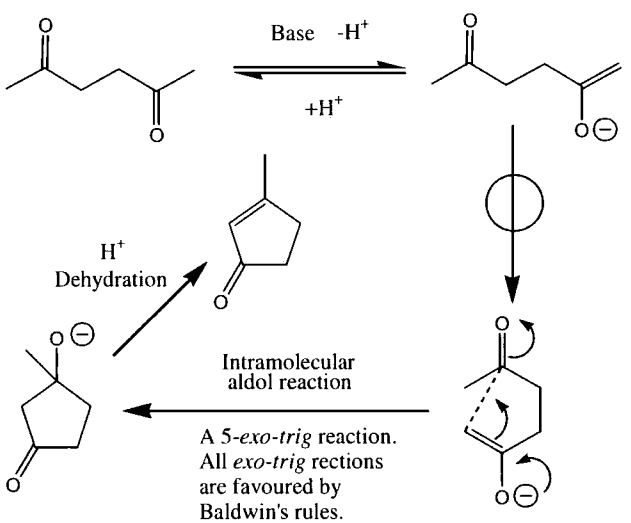
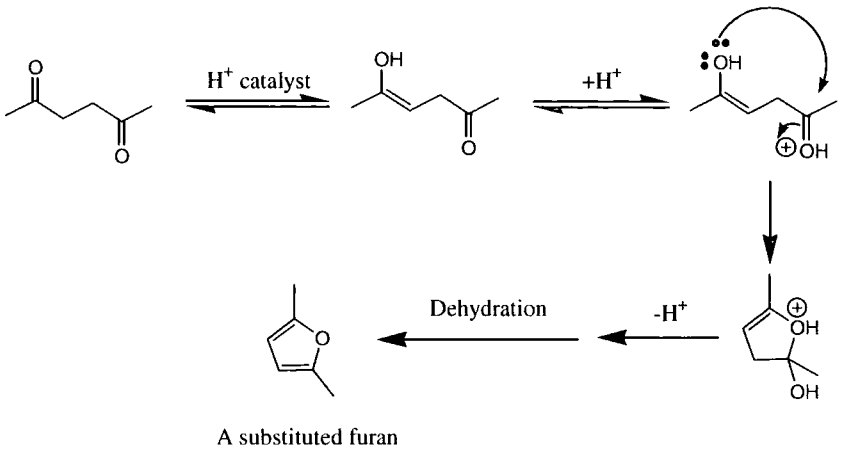


Figure 11. Cyclisation of 1,4-diketones in acidic conditions



2.2.3.2 1,4-Dicarbonyl route vs. Nazarov reaction

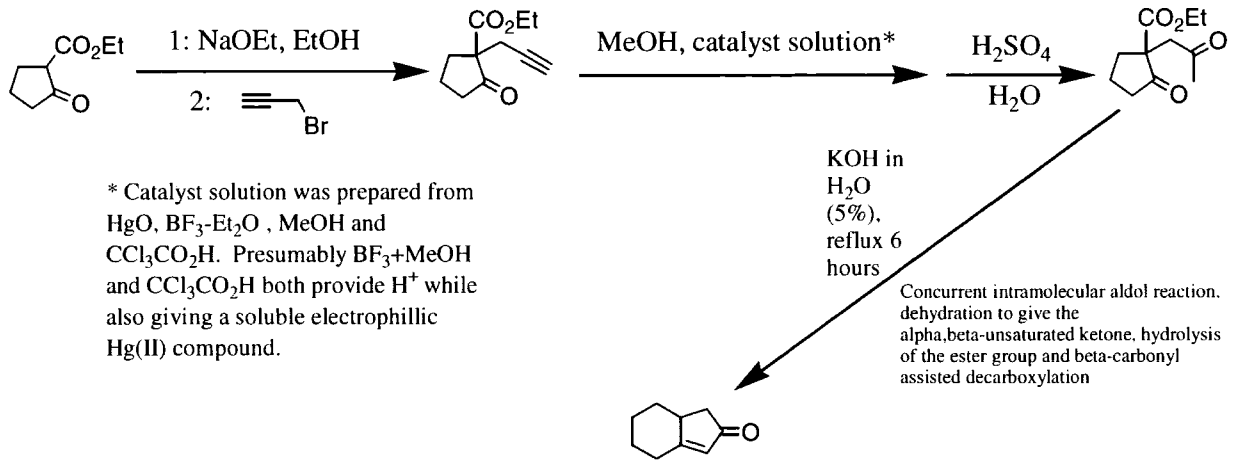
As will be seen in the next two sections, 1,4-dicarbonyl chemistry can be used to prepare cyclopent-2-en-1-ones annulated at the 3,4-position, for example bicyclo[4:3:0]non-6-en-8-one (Figure 12). For the generation of cyclopent-2-en-1-ones annulated at the 2,3- position, the Nazarov reaction is a procedurally simpler synthetic method and would commonly be preferred. Nazarov, and the closely related aliphatic Friedel-Crafts chemistry, is dealt with fully later in this chapter.

2.2.3.3 Cyclopentenone annellation utilising a 1,4-diketone cyclisation

An early example of the use of 1,4-diketones for the production of a useful cyclopentenone is given by the original synthesis of bicyclo[4:3:0]non-6-en-8-one by Islam and Raphael (Figure 12).[16] The method of preparing the requisite 1,4-diketone through propargylation of a 3-ketoester enolate anion followed by mercury catalysed alkyne hydrolysis (actually methanolysis, presumably to give the ketone acetal, followed by acidic aqueous workup) is a round-about method* and would probably now be replaced by a bromoacetone-enamine reaction (see below). However, the method of cyclising the diketone by heating for six hours in dilute (5%) aqueous KOH has been copied by later workers[21], sometimes with minor variations such as substituting ethanol for water.[17] Occasionally other bases have been used. For example Rigby, Moore and Rege employed NaH in refluxing toluene to effect the 1,4-diketone to cyclopentenone transformation as a step in annelating a cyclopentenone unit onto a pre-existing complex bicyclic entity.[18]

* Interestingly, Nazarov who was also working at around this time used mercury-catalysed alkyne hydrolysis to prepare divinyl ketones which immediately cyclised by the reaction now named after him. This is another method of synthesising cyclopentenones, although other ways of preparing the divinyl ketone precursors are now generally used. The Nazarov reaction is discussed in section 2.2.6, and particularly in subsection 2.2.6.3.

Figure 12. Original preparation of bicyclo[4.3.0]non-6-en-8-one

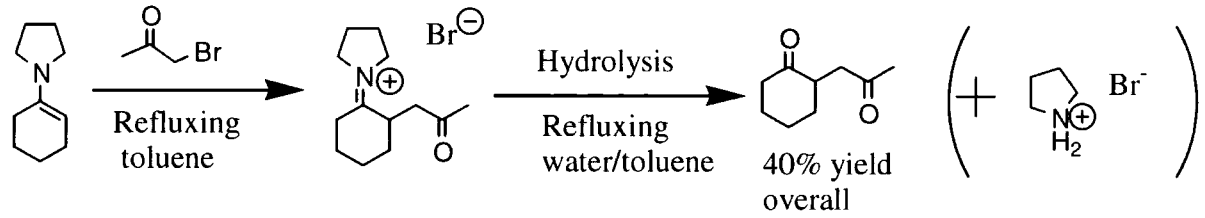


Bicyclo[4.3.0]non-6-en-8-one

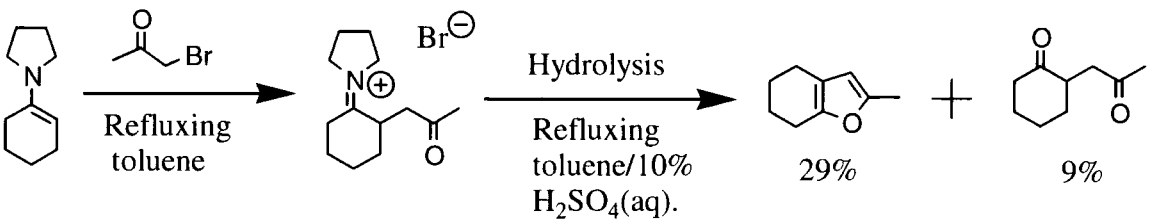
2.2.3.4 Use of bromoacetone in the preparation of cyclopentenones

Bromoacetone can be used in the preparation of 1,4-diketones.[19] One method is to react bromoacetone with an enamine, which is then hydrolysed under acidic conditions, but not too acidic or the diketone will cyclise to give a furan. The problem of accidentally producing a furan is illustrated by the first paper to be published on the reaction between bromoacetone and enamines. Baumgarten, Creger and Villars reacted cyclohexanone pyrrolidine enamine with bromoacetone, as shown in Figure 13.[20] The same reaction was also tried using bromomethyl phenyl ketone. The desired compound, 1-(2-oxocyclohexyl)propanone, was produced from the intermediate quaternary imminium bromide by hydrolysis and, although such hydrolyses are acid catalysed, the use of acid was not found to be satisfactory in this case because it catalysed cyclisation and production of the furan (7-oxa-8-methylbicyclo[4.3.0]non-1^6,8-diene).

Figure 13. A bromoacetone enamine reaction



Carrying out the hydrolysis step with an aqueous acid resulted in the production of more or less of the furan cyclisation product. The use of hot 10% H_2SO_4 resulted in an overall yield of 29% furan and 9% cyclohexanone.



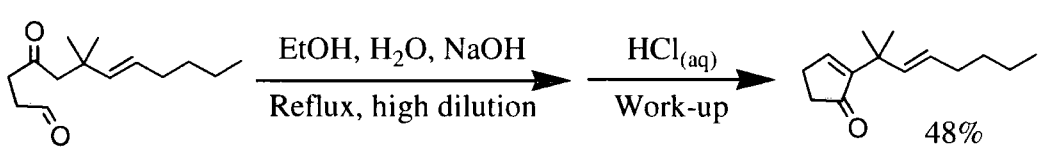
DeBoer and Ellwanger required bicyclo[4:3:0]non-6-en-8-one for a study of Baeyer-Villiger oxidation.[21] They prepared it by combining Baumgarten, Creger and Villars' method of synthesising 1-(2-oxocyclohexyl)propanone[20] (see above), except using a morpholine rather than a pyrrolidine enamine, followed by cyclisation under basic conditions using the method of Islam and Raphael (also see above).[16] The synthesis of 1-(2-oxocyclohexyl)propanone gave 21% yield (substantially lower than the 40% of Baumgarten *et al*) and the cyclisation to bicyclo[4:3:0]non-6-en-8-one proceeded with a good yield of 88%.

For a further example of the use of bromoacetone to construct a 1,4-dicarbonyl compound which is then converted into a cyclopentenone, see refs. 22 and, particularly, 23.

2.2.3.5 Cyclopentenones from 4-ketoaldehydes

4-ketoaldehydes can be cyclised to cyclopentenones in the same way as can 1,4-diketones. For example, the ketoaldehyde shown in Figure 14 was cyclised by refluxing in ethanolic sodium hydroxide.[24] High dilution was used, presumably to reduce the probability of any intermolecular reactions which might arise because of the high reactivity of aldehydes towards nucleophillic attack.

Figure 14. Cyclisation of a 4-ketoaldehyde

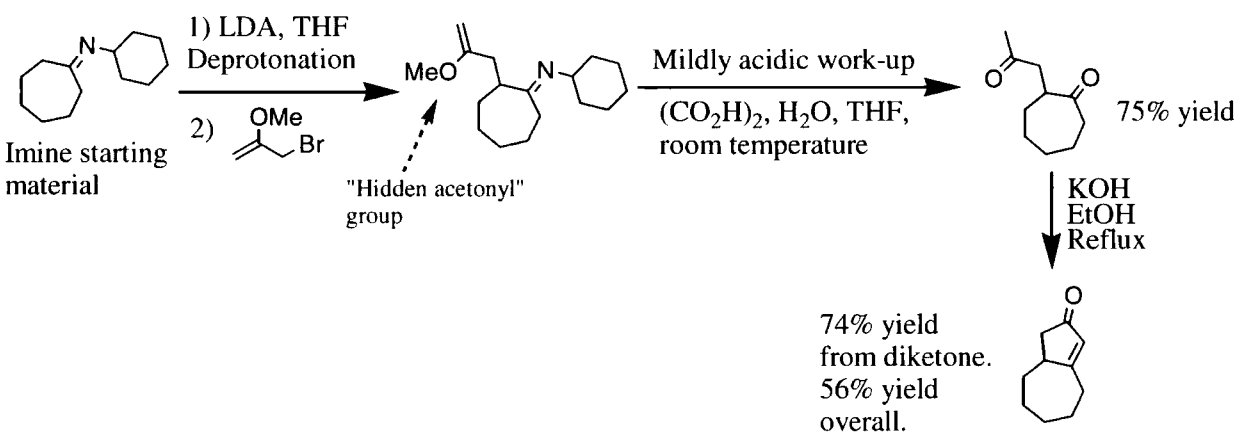


The reaction between bromoacetone and an enamine is a practical route to 4-ketoaldehydes, but only if steps are taken to moderate the reaction. The problem is discussed in a short but very useful paper by Acholonu and Wedegaertner.[25] They found that the high reactivity of aldehyde enamines tended to cause two problems, N-alkylation and tar production, during the reaction with bromoacetone. These problems were largely eliminated by simultaneously using an enamine derived from an unusually bulky amine (e.g., diisobutyl amine instead of piperidine) and using a long (48 - 96 h) reaction time at room temperature rather than refluxing. By the use of these two techniques, Acholonu and Wedegaertner raised the yield of the synthesis of 2-isopropyl-4-oxypentanal from 5% to 60%.

2.2.3.6 Preparation of 1,4-diketones and cyclopentenones using 2-methoxyallyl bromide

2-methoxyallyl bromide has been used as an alternative to bromoacetone as an acetonylating agent.[26] It gives cleaner reactions and higher yields than the corresponding reactions with bromoacetone. Jacobson, Raths and McDonald performed a valuable investigation into the use of 2-methoxyallyl bromide as an alkylating agent and they demonstrated its potential for the synthesis of 1,4-diketones and various other compounds.[15] Several of the diketones were cyclised to cyclopentenones using base to illustrate the usefulness of 2-methoxyallyl bromide as a five-carbon ring annelating reagent. Figure 15 gives one example of the reactions investigated by Jacobson, Raths and McDonald.

Figure 15. Cyclopentenone synthesis using 2-methoxyallyl bromide



The acidic workup necessary to convert the enol ether group to the required ketone group is mild and Jacobson, Raths and McDonald do not report any problems with furan production.

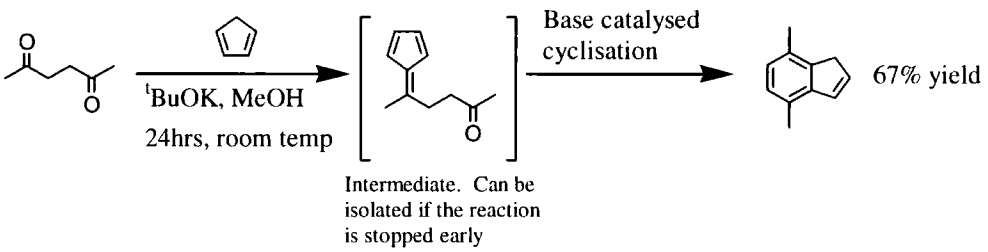
For an example of the use of 2-methoxyallyl bromide as a cyclopentenone annulation reagent in natural product chemistry, see ref. 18.

2.2.3.7 Synthesis of indenes from 1,4-dicarbonyl compounds and a related process

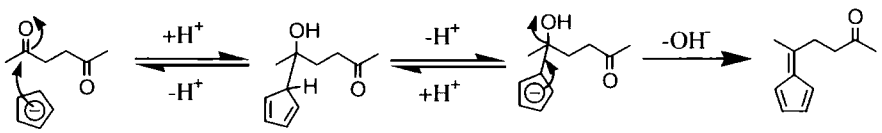
While not involving cyclopentenones, this chemistry is relevant as it involves chemistry closely associated with the cyclisation of 1,4-diketones, described above.

Coe, Vetelino and Kemp reported a novel method of synthesising indenes in 1994.[27] They discovered that while a pyrrolidine-catalysed condensation between a 1,4-diketone and cyclopentadiene gave a bis-fulvene*, an analogous reaction carried out with a potassium *tert*-butoxide catalyst gave a monofulvene which rapidly cyclised under the reaction conditions (Figure 16). The cyclisation is reminiscent of the base-induced cyclisation of a 1,5-diketone, previously illustrated in Figure 10.

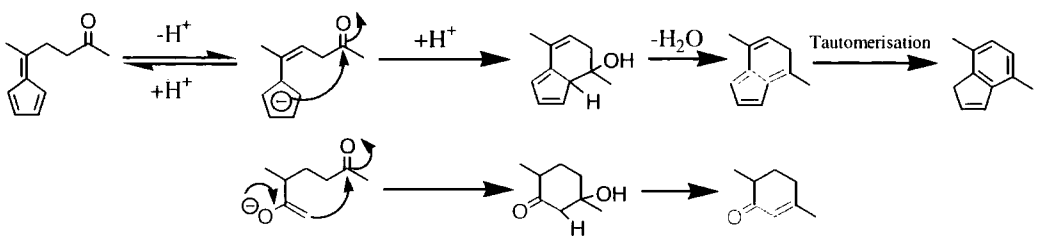
Figure 16. Preparation of indenes from 1,4-diketones



The mechanism starts with a standard fulvene condensation



The fulvene then cyclises as follows:



Analagous cyclisation of a 1,5-diketone

The reaction was extended to 4-ketocarboxylic acids.[27] The fulvenes derived from them were cyclised under basic conditions after activation of the acid group with *N,N'*-carbonyldiimidazole.

As part of an elegant synthesis of an *ansa*-bis-cyclopentadienyl ligand which selectively gave *rac*-complexes when coordinated to early transition metals, Erker and co-workers employed an

* Except under mild reaction conditions when the diketone is an alkyl-aryl ketone. The alkyl ketone unit, $CH_2C(O)R$, is converted to a fulvene but the aryl end, $CH_2C(O)Ar$, is not. See M. Könemann, G. Erker, R. Frölich, S. Kotila, *Organometallics*, **16**, 2900-2908, (1997), (bottom of p2901), and references therein.

ingenious reaction with close similarities to that described above.[28] They cyclised a mono-fulvene derived from 1-phenyl-pentane-1,4-dione* by an intramolecular nuclophillic attack of Cp^-, as above, the difference being that it was initiated by addition of Me^- (from MeLi) rather than removal of H^+. The result, after dehydration, was a cyclohexene-annulated cyclopentadiene, which was subsequently dimerised to an *ansa*-ligand *via* a radical anion formed by treatment with Ca(Hg).

2.2.4 Synthesis of cyclopentenones from cyclopentane-1,2-dione

In a short but useful paper, Ansell and Ducker describe a general method of synthesising 2-substituted cyclopent-2-en-1-ones from cyclopentane-1,2-dione.†, [29] Figure 17 shows how the synthesis proceeds. The first step is to produce 2-*iso*butoxycyclopent-2-en-1-one, an enol ether. This is reacted with a suitable Grignard reagent to give a product which then hydrolyses and tautomerises to the most thermodynamically stable double bond isomer of the required cyclopentenone.‡

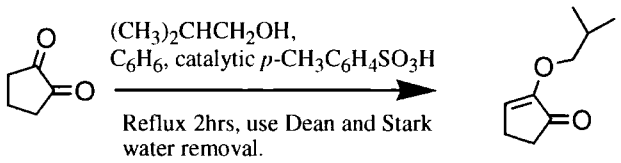
---

* The fulvene selectively formed at the non-phenyl substituted end, see footnote on previous page for more details. The formula of the fulvene was $CH_3C(C_5H_4)CH_2CH_2C(O)C_6H_5$.

† Unfortunately, cyclopentane-1,2-dione does not appear to be a current commercial product. It is not in the catalogues of five well known organic fine-chemical suppliers, a fact sufficient to make the above synthesis unattractive to the general organometallic chemist.

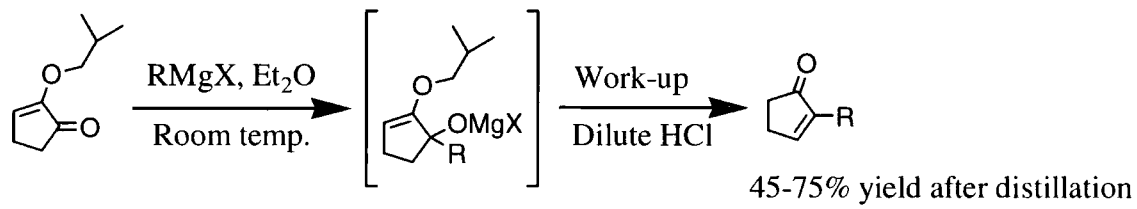
‡ Presumably, if a 1,2-disubsituted cyclopentadiene with two identical substituents is required then protection of one carbonyl group as an enol ether would not be necessary. Cyclopentane-1,2-dione should react directly with two equivalents of Grignard reagent to give a 1,2-disubstituted cyclopentane-1,2-diol. The latter should be easy to dehydrate to the cyclopentadiene. It seem likely that the same set of reactions would also work with cyclopentane-1,3-dione, which has the additional advantage that it can easily be substituted at the active 2-methylene group beforehand, if required.

Figure 17. Synthesis of cyclopentenones from cyclopentane-1,2-dione



2-*iso*butoxycyclopent-2-en-1-one
67% yield after distillation.
Stable liquid.

2-*iso*butoxycyclopent-2-en-1-one readily reacts with Grignard reagents RMgX {X= unspecified halogen, probably Br or I; R= $CH_3(CH_2)_n$, n= 0-5; $(CH_3)_2CH$; $Ph(CH_2)_n$, n= 0,2,3}. The reaction proceeds as follows:



Not isolated

45-75% yield after distillation

The above procedure has also been carried out using allyl magnesium bromide as the Grignard reagent, although the product was a cyclopentanone as dehydration gave an exo-cyclic double bond.[23]

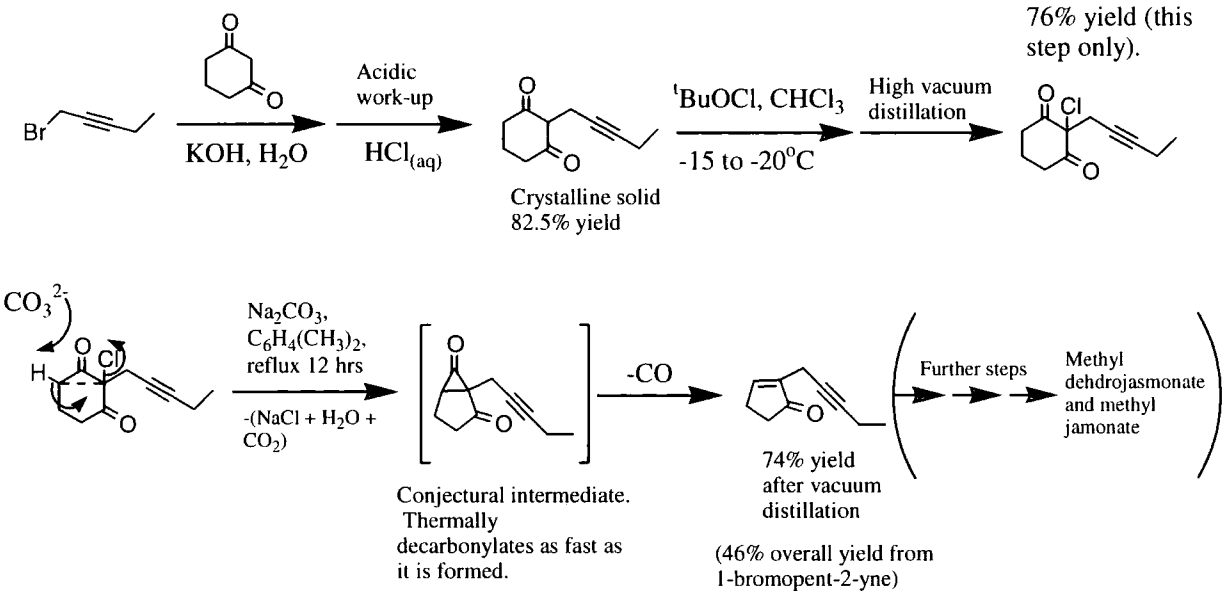
2.2.5 Synthesis of cyclopentenones from cyclohexane-1,3-dione.

Cyclohexane-1,3-dione (contains a substantial equilibrium concentration of the enol tautomer under ambient conditions) is commercially available* and is the starting material for an ingenious cyclopentenone synthesis, originally devised as a route to jasmone and related compounds.[30] The process is illustrated in Figure 18.

The key step is the ingenious base-induced dehydrochlorination-decarbonylation ring contraction. A close analogy exists between this process and the better-known Ramberg-Bäcklund reaction[31] in which an α-halosulfone with an α'-hydrogen dehydrochlorinates and cyclises to an episulfone on treatment with base. Under the reaction conditions the episulfone rapidly eliminates SO_2 to give an alkene as the isolated product.

* 1,3-cyclohexanedione £22.90/100g (Aldrich 2003-2004)

Figure 18. Synthesis of a cyclopentenone from cyclohexane-1,3-dione



The cyclohexane-1,3-dione route to has been used to synthesise at least one other cyclopentenone. 2-(prop-2-en-1-yl)cyclopent-2-en-1-one was prepared by a process similar to that described above, but using allyl bromide instead of 1-bromopent-2-yne.[23]

2.2.6 The aliphatic Friedel-Crafts reaction and the Nazarov Reaction

2.2.6.1 Introduction

Friedel-Crafts alkylation and acylation are extremely common methods of functionalising aromatic substrates. As a method of constructing non-aromatic compounds, Friedel-Crafts reactions are not so widely known even though they may be of great utility. Aliphatic Friedel-Crafts reactions have been used to prepare a substantial number of substituted cyclopentenones and related compounds. The aliphatic Friedel-Crafts reaction is also often used to prepare divinyl ketones, these being readily converted to cyclopentenones by the Nazarov reaction, discussed later in this chapter. Indeed, the divinyl ketone synthesis and Nazarov cyclisation are normally carried out simultaneously in a seamless one-pot one-step process, eminently suited to the cheap bulk synthesis of many cyclopentenones.

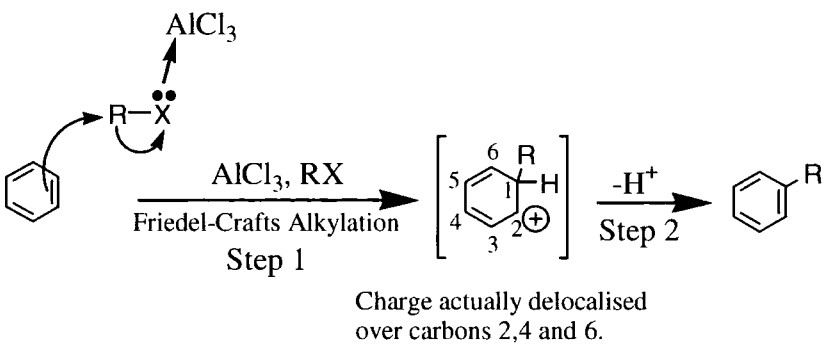
2.2.6.2 Aliphatic Friedel-Crafts reactions

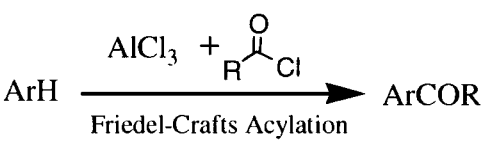
Aliphatic Friedel-Crafts acylations have been reviewed.[32, 33] A useful summary of aliphatic and aromatic Friedel-Crafts reactions and related processes is also available.[34]

Figure 19 shows the familiar aromatic Friedel-Crafts reaction and Figure 20 illustrates the aliphatic analogue. The aliphatic variant is closely similar to the aromatic in that the reagent is an alkyl or acyl compound which is converted to an electrophilic carbanionic species by

protonation, or by complexation to a Lewis acid. The electrophile then attacks a C-C π-bond in the substrate, which for the aliphatic variant may be an alkene or alkyne. There is an important difference between the aliphatic and aromatic reactions in the next step (step 2 in the Figures); with an aromatic substrate, re-aromatisation forces loss of H^+, but with an aliphatic substrate there may be either loss of H^+ (possibly followed by a double bond isomerisation), or there may be capture of a nucleophile. In the latter case, a saturated product is formed and the overall reaction is one of addition to the double bond. For an example of an aliphatic Friedel-Crafts reaction in which changing the reaction conditions by lowering the reaction temperature and changing the electrophile precursor from an acyl chloride to a bromide caused H^+ abstraction to swap from being favoured to disfavoured relative to halide capture, see ref. 47.

Figure 19. Aromatic Friedel-Crafts reactions





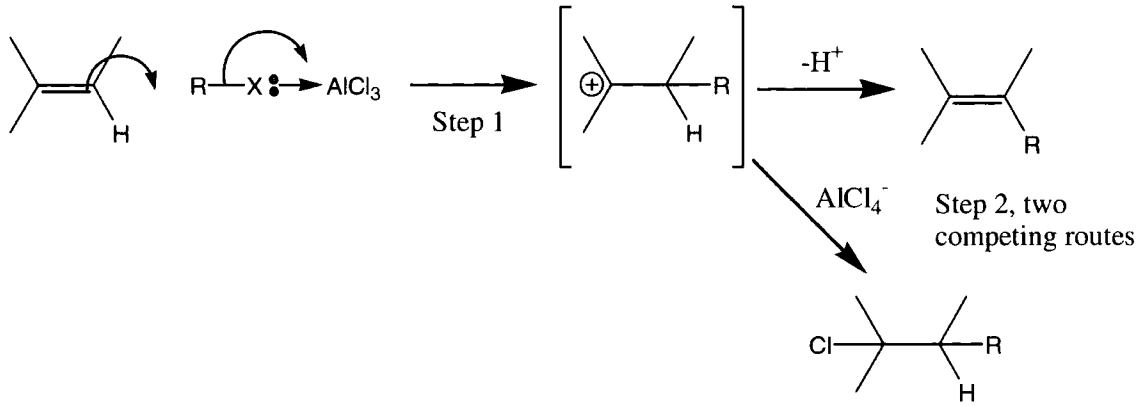
Other reagents for alkylation include alcohols + protic acid or alkene + H^+ + Lewis acid.

Acylation may also be achieved with carboxylic acids or anhydrides with a Lewis acid being required in either case.

Due to the strong bonding in the complex formed between $AlCl_3$ (or other Lewis acid) with carbonyl groups, it is normally necessary to use > 1 equivalent of the acid for acylation. For alkylation, the acid acts catalytically.

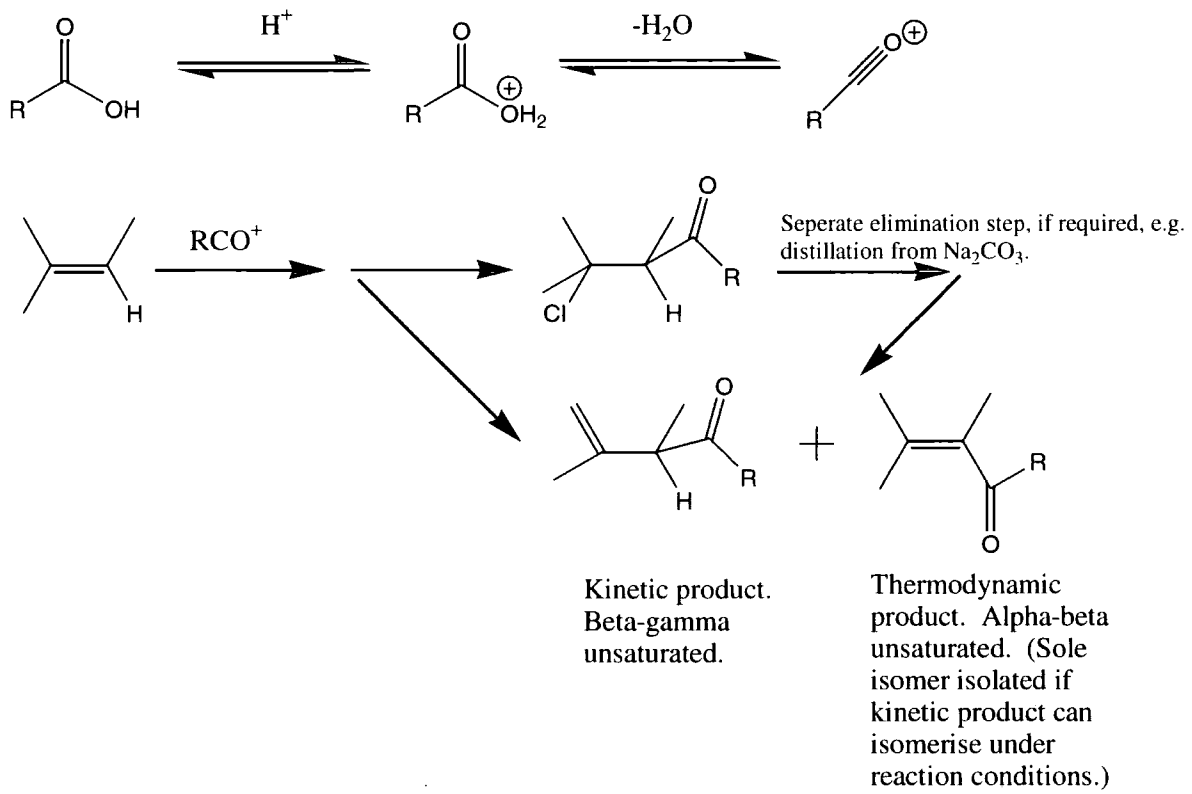
Figure 20. Aliphatic Friedel-Crafts reactions

Alkylation



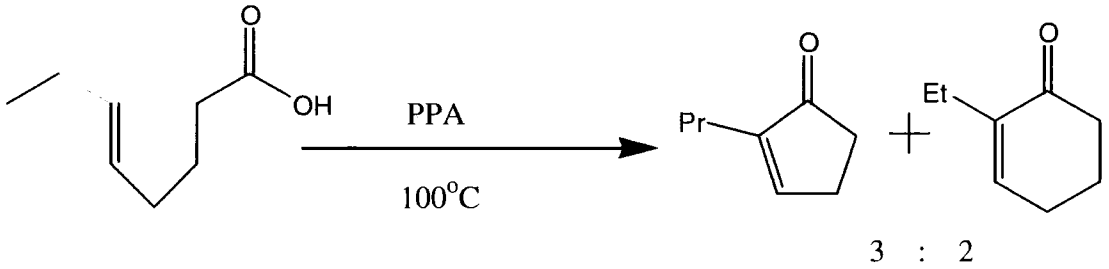
Acylation

Formation of acyllium cation, e.g. from carboxylic acid and strong protic acid:



Friedel-Crafts alkylation is only of limited utility due to the propensity of carbo-cations to rearrange and due to the ease of poly-alkylation. Acylations give better results and can be carried out intra-molecularly to produce cyclic products. Figure 21 shows an early example whereby a 5,6-unsaturated carboxylic acid undergoes intramolecular condensation in hot polyphosphoric acid (PPA, see glossary) to produce a mixture of 2-alkyl-cyclo(penta and hexa)-2-en-1-ones.[35]

Figure 21. An early cyclopentenone-producing intramolecular Friedel-Crafts reaction



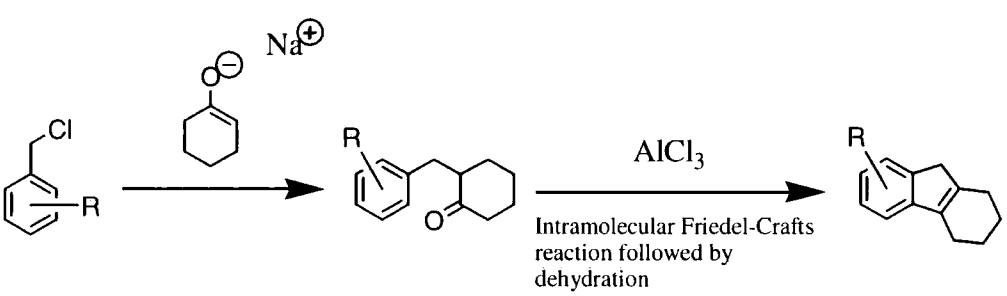
The powerfully acidic conditions necessary for Friedel-Crafts reactions often cause side reactions such as cationic polymerisation of the alkene. Reactive alkenes, e.g. 1,3-dienes, could well be converted entirely to resinous material. The yields of aliphatic Friedel-Crafts reactions are often in the range 40 – 80 %.

Aliphatic Friedel-Crafts acylation is an extremely important method of synthesising divinyl ketones, these being substrates for the Nazarov cyclisation. Indeed, is in this context that the aliphatic Friedel-Crafts reaction is of most use to the chemist wishing to synthesise cyclopentenones. Before discussing the Nazarov reaction in some detail, the use of the aromatic Friedel-Crafts reaction for the synthesis of indenes and fluorenes will be briefly discussed.

2.2.6.2.1 The use of the aromatic Friedel-Crafts reaction to synthesise benzene-annelated cyclopentadienes.

Although this section is principally concerned with aliphatic Friedel-Crafts reactions in the synthesis of cyclopentenones, it is relevant to note that the aromatic Friedel-Crafts reaction can be used to generate indenes, fluorenes and related systems.[36] The requisite five-membered ring is formed by an intramolecular Friedel-Crafts alkylation between a benzene ring and a pendant carbonyl group.[37] A recent example exemplifying the method is given by Rausch and co-workers who utilised the following scheme (Figure 22) to synthesise substituted tetrahydrofluorenes, afterwards elaborated into *ansa*-ligands.[38]

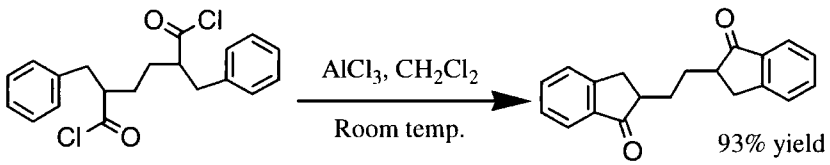
Figure 22. Synthesis of tetrahydrofluorenes using an intramolecular Friedel-Crafts reaction



R= H, 1-Me, 2-Me, 3-Me, 4-Me, 1,4-Dimethyl, 2,5-Dimethyl, 4-^{t}Bu.

Schaverien has recently used an intramolecular Friedel-Crafts acylation in the construction of ethylene bis(2-indenyl) ligands.[39] The Friedel-Crafts cyclisation step is shown in Figure 23. The reaction was carried out on a large (~500g) scale with no reported problems; although vigorous HCl evolution was noticed, there was no appreciable temperature rise. This illustrates the frequent suitability of Friedel-Crafts reactions for bulk syntheses.

Figure 23. Schaverien synthesis of ethylene bis(2-indenyl) ligands: The Friedel-Crafts cyclisation step

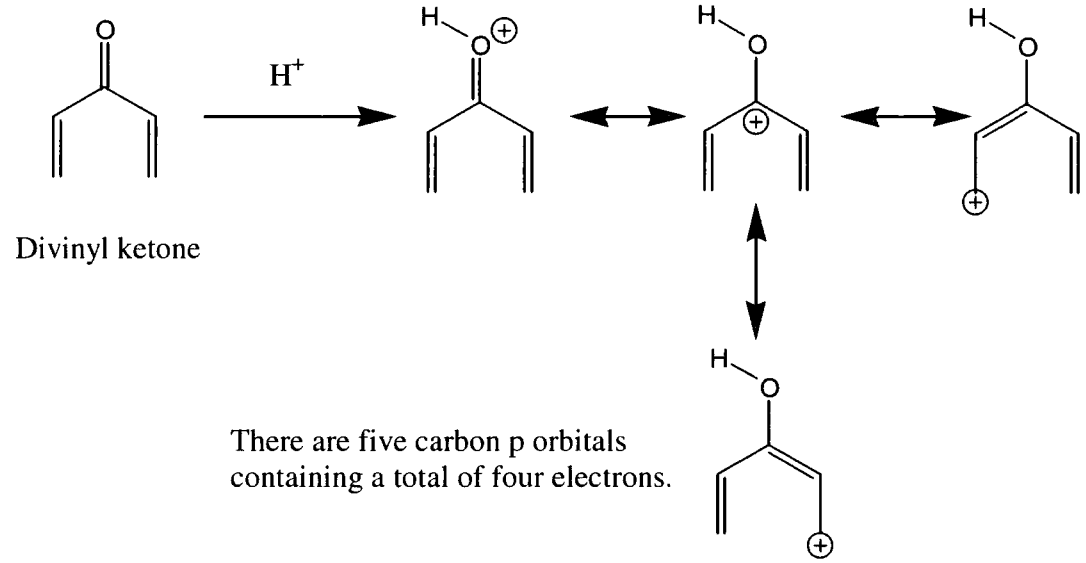


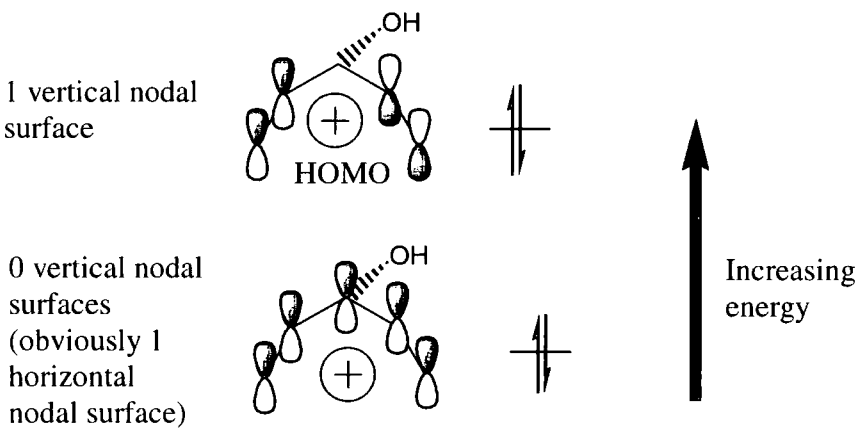
2.2.6.3 The Nazarov reaction.

The Nazarov reaction involves the electrocyclic ring closure of a protonated divinyl ketone to give a cyclopentenone. The extremely high reactivity of divinyl ketones, and their ready polymerisation, means that they are not normally isolated, but are instead synthesised under acidic conditions and allowed to cyclise as formed. Divinyl ketone synthesis is often carried out via an aliphatic Friedel-Crafts reaction, the overall result being the synthesis of a cyclopent-2-en-1-one (which may be highly substituted and annelated to one or two further rings) from simple, cheap precursors in a single step. Thus the process has been very widely used.

Nazarov reactions have been reviewed.[40 - 42] A particularly lucid explanation of the mechanism of the reaction is also available.[43] Information on divinyl ketone and some substituted analogues, including useful references, is extant.[44]

Figure 24. Mechanism of the Nazarov reaction





Under normal (thermal) conditions, conrotatory ring closure takes place.

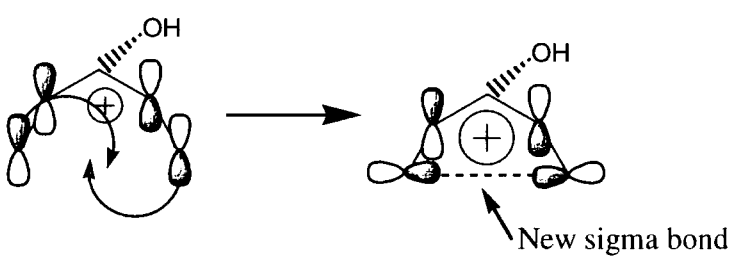
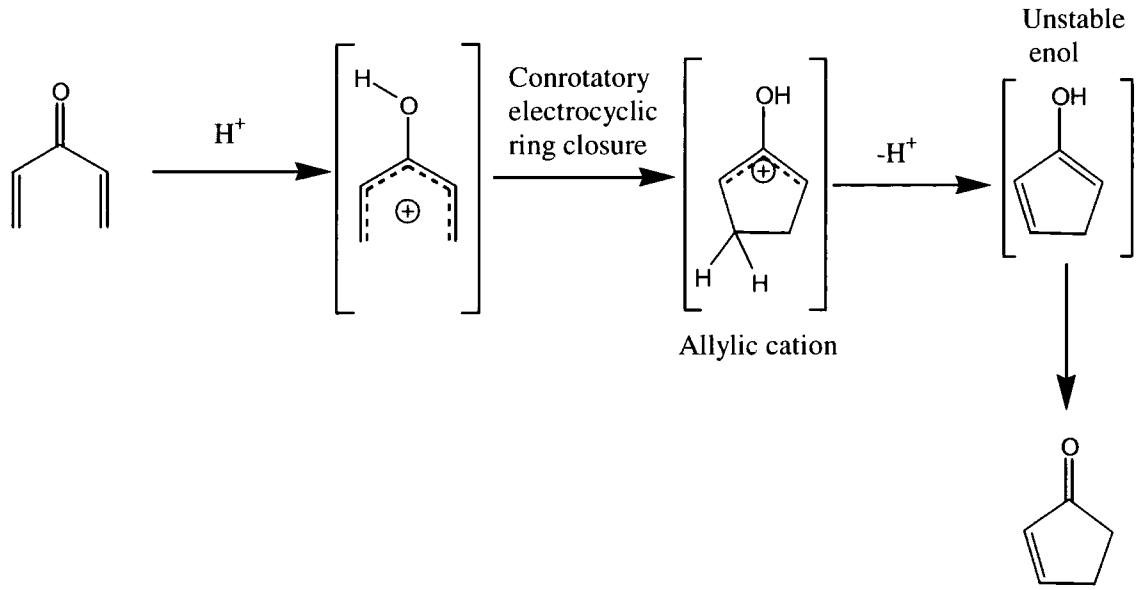


Figure 24 continued on next page

Figure 24, continued



Nazarov cyclisations have been photochemically induced in a disrotatory fashion for mechanistic studies.[41]

Divinyl ketones can prepared in numerous ways, and there are numerous variations of the Nazarov reaction which employ the ability of silyl or stannyl auxiliaries to stabilise β-carbocations as a means of achieving superior regioselectivity. The use of precursors which may be converted to divinyl ketones (which immediately cyclise) under mild conditions allows utilisation of the diastereoselectivity of the pericyclic reaction, as mild conditions reduce the possibility of isomerisation of the product. However, elegant stereoselective syntheses of cyclopenenones are not relevant if the final product is a flat-ringed cyclopentadienyl compound in which such stereo-features are not present.* Thus, reactions of this type will not be considered further. Instead, the more useful (to the organometallic chemist), coupled aliphatic Friedel-Crafts-Nazarov process will be discussed.

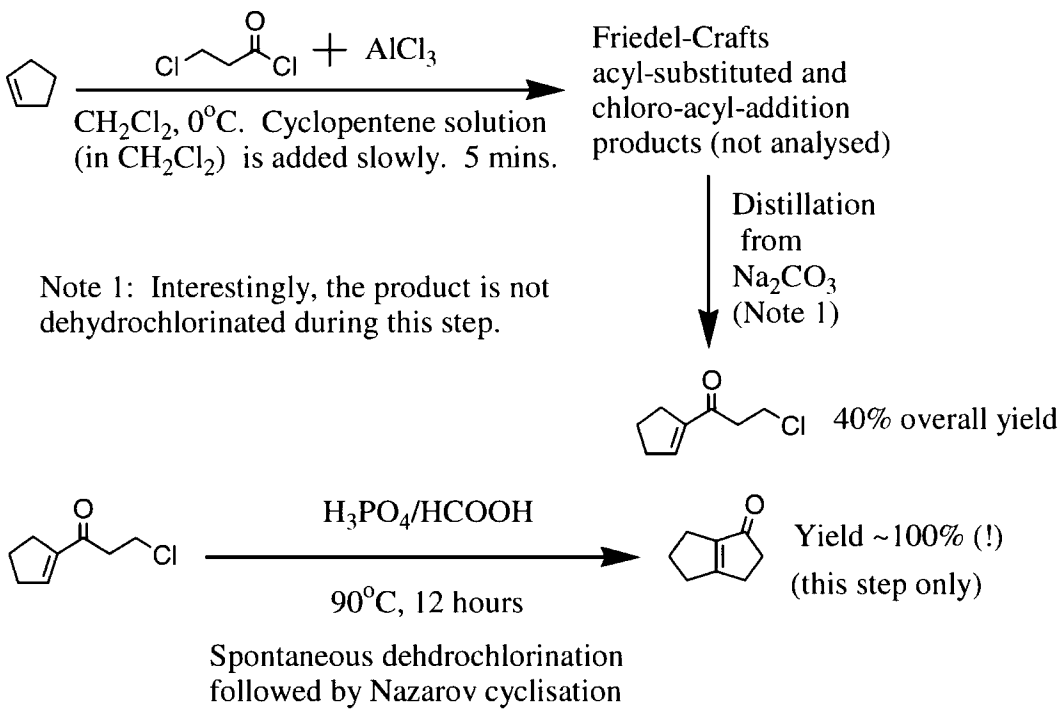
* Suitably controlled Nazarov reactions, using mild conditions to prevent isomerisation, may give cyclopentenones with enhanced yields of isomers in which substituents on the ring carbons are in particular cis or trans relationships. Obviously, if the ring is converted to a cyclopentadiene then these cis/trans distinctions disappear. However, it is conceivable that the stereochemistry around the ring carbons in a cyclopentenone substrate could be used to direct the synthesis of a cyclopentadiene with defined stereochemistry around atoms α to the ring carbons, or further away. The author has not yet seen any examples of this having been attempted.

2.2.6.3.1 Sequential aliphatic Friedel-Crafts – Nazarov reactions.

2.2.6.3.1.1 Use of elimination reactions to prepare the divinyl ketone intermediates.

β-chloro ketones are easily dehydrochlorinated to α,β-unsaturated ketones and this provides a route to the Nazarov cyclisation.[45] Friedel-Crafts acylation of cyclopentene with 3-chloropropionyl chloride (a cheap commercial product) gave an α,β-unsaturated-β'-chloro ketone* which dehydrochlorinated and cyclised when heated in a solution of phosphoric acid in formic acid (a typical acidic Nazarov catalyst).[46] The reaction is illustrated in Figure 25. The process takes two steps, or three if the sodium carbonate purification is counted. The apparent 100% yield in the final step (5g chloroketone gave 4g bicyclo[3.3.0]oct-1(5)-en-2-one), and the inability of sodium carbonate to completely dehydrochlorinate the chloroketone are not commented on in the original paper.[46]

Figure 25. Preparation of a divinyl ketone precursor using an aliphatic Friedel-Crafts reaction and subsequent Nazarov cyclisation[46]



It might be thought that the cyclisation could be carried out using a Friedel-Crafts reaction initiated using $AlCl_3$ or another Lewis acid. This would, however, be unlikely to work, as strong coordination to the carbonyl oxygen would draw electrons out of the C=C bond and powerfully deactivate the latter towards electrophillic attack.

* Presumed; it was not analysed.

α,β-unsaturated ketones with a β'-O or –N substituent have also been prepared and found to undergo elimination and Nazarov cyclistion under acidic conditions.[40] They have been prepared by various methods, but the reactions are of more interest to the synthetic organic chemist than the organometallic chemist, so they will not be considered further.

2.2.6.3.1.2 Direct synthesis of the divinyl ketone intermediates.

The use of the aliphatic Friedel-Crafts reaction to assemble a divinyl ketone which then cyclises *in situ* is a procedurally simple method of assembling substituted cyclopentanones in moderate yield (typically 40 to 60 %) from low cost starting materials. It is hard to find a better method of cheaply and easily churning out large quantities of substituted, particularly annelated, cyclopent-2-en-1-ones. The technique has been much exploited as a route to cyclopentadienes. The starting materials required for the reaction are an alkene, or alkene precursor, and an α,β-unsaturated carboxylic acid derivative. Any acid derivative which will give an acylium ion under the reaction conditions can be used. Alcohols may be used as an alkene substitute as they eliminate water under the influence of the powerfully acidic and dehydrating Nazarov reaction conditions. α,β-unsaturated esters break down to give an acid and alkene which then react; indeed in many examples esters give better yields than other starting materials.[41]

The usual reaction conditions for the sequential aliphatic Friedel-Crafts - Nazarov reaction involve mixing the reactants with a large excess of warm polyphosphoric acid, typically at 60°C. Some of the earlier experiments used the more reactive catalyst $AlCl_3$, but low reaction temperatures (-78 °C) and the use of acyl bromides, rather than the less reactive chlorides, were found necessary to prevent the formation of an acylic chloroketone as the main product.[47] The chloroketones or, to be more precise, β-chloro-α'β'-unsaturated ketones, were formed by the capture of Cl^- by the anion resulting from attack of the acyllium ion on the alkene. The overall process was one of addition of acyl chloride to the alkene, a reaction discussed in the section on the aliphatic Friedel-Crafts reaction, above.

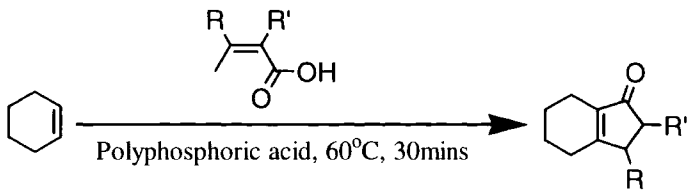
Cyclopentenones with numerous different substitution patterns have been prepared by the Aliphatic Friedel-Crafts Nazarov route. A large number of examples are presented in various review articles.[40 - 42] Due to constraints of space, and because the material is so well covered elsewhere, only a couple of syntheses will be given here. The examples have been chosen because they are closely related to the experimental work described later in this thesis.

Cyclopent-2-en-1-ones annulated to another ring across the 2,3-position are easily prepared by the aliphatic Friedel-Crafts Nazarov process.* As an example, cyclohexene and acrylic or

* For the synthesis of cyclopent-2-en-1-ones annulated across the 3,4 position, base induced cyclisations of 1,4-diketones, easily prepared by the use of bromoacetone or 2-methoxyallyl bromide, are suitable. Syntheses of this type were discussed earlier in this chapter.

methyl-substituted acrylic acids have been reacted together in warm polyphosphoric acid to prepare cyclopent-2-en-1-ones for subsequent elaboration into cyclopentadienyl ligands.[7, 8, 10]

Figure 26. Sequential aliphatic Friedel-Crafts Nazarov synthesis of cyclopentenones: examples



R	R'	Name of acid	Yield /%
H	H	Acrylic	20
Me	H	Crotonic	36
Me	Me	Tiglic	24

(Data in the above table is taken from ref. 7. Refs. 8 and 10 refer to the reaction using crotonic acid and give improved reaction conditions, raising the yield to 55%.)

2.2.6.3.1.2.1 Ester Byproducts

The reaction of carboxylic acids (including α,β-unsaturated carboxylic acids) with various alkenes in the presence of polyphosphoric acid can result in the formation of esters.[48, 49] For example, in the work discussed later in this thesis, crotonic acid was reacted with cyclohexene in warm polyphosphoric acid. It was found that the cyclopentenone product, (9-methylbicyclo[4.3.0]non-1(6)-en-7-one*) was always contaminated by a substantial fraction of cyclohexyl crotonate, almost impossible to remove by distillation. It interesting to note the dynamic nature of the production of this byproduct, as esters are themselves disassembled and converted to cyclopentenones by the action of polyphosphoric acid.

Ester formation appears to take place by a mechanism involving an initial protonation of the alkene.[48, 49] The resulting carbocation can then add to the carboxylic acid at O; loss of H^+ from the carboxylate OH then completes the ester synthesis. A proportion of the carbo-cation may react with alkene to form a dimer,[48] or more highly polymerised tarry resinous substances.

Careful optimisation of reaction conditions can result in ester formation predominating and reaching a synthetically useful level. Ndong Mebah and co-workers managed to obtain good yields of methacrylate esters of cycloalkenes by this technique.[49]

2.2.6.3.1.3 Nazarov cyclopentenone production from methylcyclopentane and other alkenes

Alkanes can be acylated under Friedel-Crafts conditions.[50, 51] Acylation is able to take place

* Alternatively named 3-methyl-2,3,4,5,6,7-hexahydro-1*H*-indene-1-one or sometimes 3-methyl-4,5,6,7-tetrahydroindan-1-one.

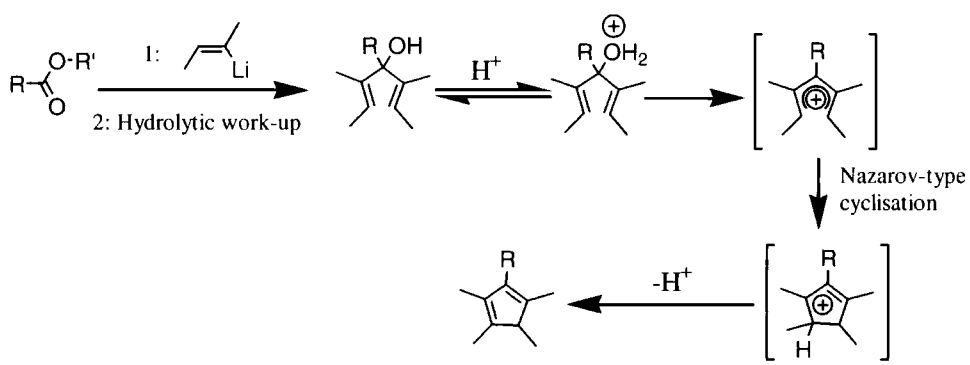
because hydride transfer from the alkane to a cationic species (for example H^+, with the formation of molecular hydrogen, in sufficiently strong acids, e.g. $H[AlCl_3OH]$ {i.e. $AlCl_3$ + H_2O} followed by loss of H^+ gives an alkene in situ. The alkene is then acylated by the usual aliphatic Friedel-Crafts mechanism.

Santelli and co-workers published an interesting and very detailed paper on the preparation of monocyclic and bicyclic cyclopent-2-en-1-ones from saturated alkanes (methylcyclopentane, methylcyclohexane, 2-methylbutane or even diesel fuel {!!}) and α,β-unsaturated acyl chlorides.[51] Modified Friedel-Crafts Nazarov conditions were used and gave yields of up to 60 %, very good for this type of reaction and very attractive given the cheapness of the starting materials. However, most (but not all) of the cyclopenenones synthesised had dialkyl substitution on one ring carbon and could thus only give cyclopentadienyl ligands if an alkyl shift was carried out.

2.2.6.3.2 A cyclisation analogous to the Nazarov reaction

An ingenious synthesis based on the Nazarov-like cyclisation of a diallyl alcohol, very suitable for the preparation of 1-alkyl-2,3,4,5-tetramethylcyclopentadienes, has been much used.[52] The generalised procedure is shown in Figure 27. It should be noted that mechanism of the electrocyclic ring-closure step is essentially identical to that of the Nazarov reaction.

Figure 27. The cyclisation of substituted penta-1,2-dien-3-ols



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3 Experimental work

3.1 Abbreviations and names of compounds

In the interests of clarity and conciseness, the compounds discussed in this chapter are referred to by abbreviations. A list of the structural formulae, systematic names and abbreviated names for these compounds is given below.

For compounds based on the hydroindene skeleton, arene nomenclature will be used rather than forming names on the alicyclic system. Further information on the derivation of systematic names for hydroindenes will be found in Appendix 1.

Figure 1. Ketone 1, HK1 (3-methyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-one)

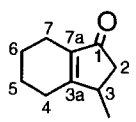
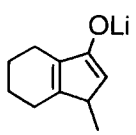


Figure 2. Lithiated Ketone 1, LiK1



(Carbons are numbered as for HK1, above.)

Figure 3. Cyclopentadiene 1, HCp1 (1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene)

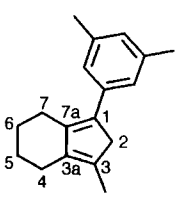


Figure 4. (Trimethylsilyl)cyclopentadiene 1, TMSCp1 ((*R,S*)-1-(3,5-dimethylphenyl)-2-(trimethylsilyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene)

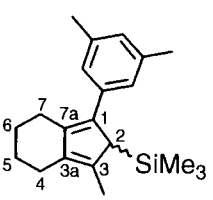
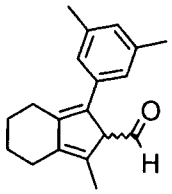
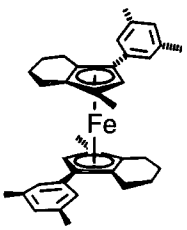


Figure 5. Cyclopentadiene 2, HCp2 ((*R,S*)-1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2*H*-indene)



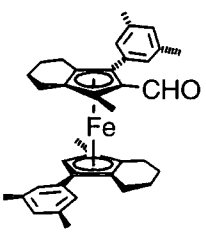
HCp2 is equivalent to (formyl)Cp1, i.e. Cp1CHO.

Figure 6. $(Cp1)_2Fe$ (*bis*-η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II))



The *meso* diastereomer is shown.

Figure 7. Cp1Cp2Fe (η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]-η^5-[1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II))



The Cp1Cp2Fe dealt with in this thesis consisted of a racemic mixture of the two enantiomers of *pseudomeso*-{η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]-η^5-[1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II)}

Notes on Figure 7

The term *pseudomeso* indicates that the structure would be a *meso* stereoisomer if it were not for the presence of a minor substituent, the formyl group in this case. The presence of the formyl substituent on only one of the indenyl groups renders them non-identical and removes the centre of inversion in the molecule. Thus the molecule shown is chiral, but, as will be seen in the experimental section, it was formed as a racemate.

Figure 8. Cp1TiCl$_3$ (η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]trichlorotitanium(IV))

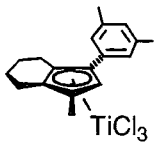
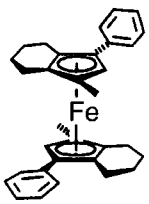


Figure 9. (Cp3)$_2$Fe (*bis*-(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl)iron(II))



The *meso* diastereomer is shown.

3.2 Overview of experimental work

3.2.1 Aim of the project

The original aim of the experimental work was to produce a novel bulky substituted chiral *ansa* cyclopentadienyl ligand and enantiopure early transition metal and lanthanide complexes thereof. The ligand was preferably to have homotopic faces (class III), not contain any labile or easily degraded groups and have a short (preferably two carbon atom) bridge since long, flexible bridges give complexes with poor catalytic activity.[1] The ligand would need to be bulky to exert stereochemical control over the reactions of its complexes and to prevent dimerisation in the lanthanidocenes it was hoped to prepare. However, due to various factors including failed experiments and illness, the work rather lost direction and this object was not achieved.

To facilitate the early stages of the project, it was decided to begin by repeating and then extending some work previously done at Durham.[2, 3] To this end, an aliphatic-Friedel-Crafts Nazarov reaction was used to prepare 3-methyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-one which was subsequently used as the starting material for the actual or attempted preparation of a number of cyclopentadienes and complexes thereof This aspect of the work was the most successful and is written-up in this thesis.

Later stages in the experimental work were troubled by unsuccessful experiments and poor data and suffered as a result of the author being afflicted by health problems. As a result, it has been decided to exclude them from presentation in this thesis.

3.3 Discussion of experimental work

3.3.1 Introduction

The first part of the experimental work attempted was an extension of research previously done in Durham[2, 3] and North Carolina[4] on the preparation and properties of various substituted tetrahydroindenyl complexes. This previous research involved the preparation of tetrahydroindanones using a sequential aliphatic Friedel-Crafts reaction – Nazarov Cyclisation (see section 3.2.6, and subsections therein). After separation, the tetrahydroindaneones were converted to tetrahydroindenes by treatment with a Grignard or organo-lithium reagent followed by facile dehydration (see section 3.2.2.1). The tetrahydroindenes were easily complexed by heating with $Fe_2(CO)_9$ or by deprotonation and reaction with $FeCl_2$ or $ZrCl_4$.

During the course of the present work, a new tetrahydroindene, 1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene (abbreviation HCp1) was prepared. Also synthesised was a trimethylsilyl derivative, (R,S)-1-(3,5-dimethylphenyl)-2-(trimethylsilyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene (code TMSCp1) and both were used to prepare metal derivatives.

3.3.2 Synthesis of 3-methyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-one (HK1)

3.3.2.1 Initial efforts at synthesis

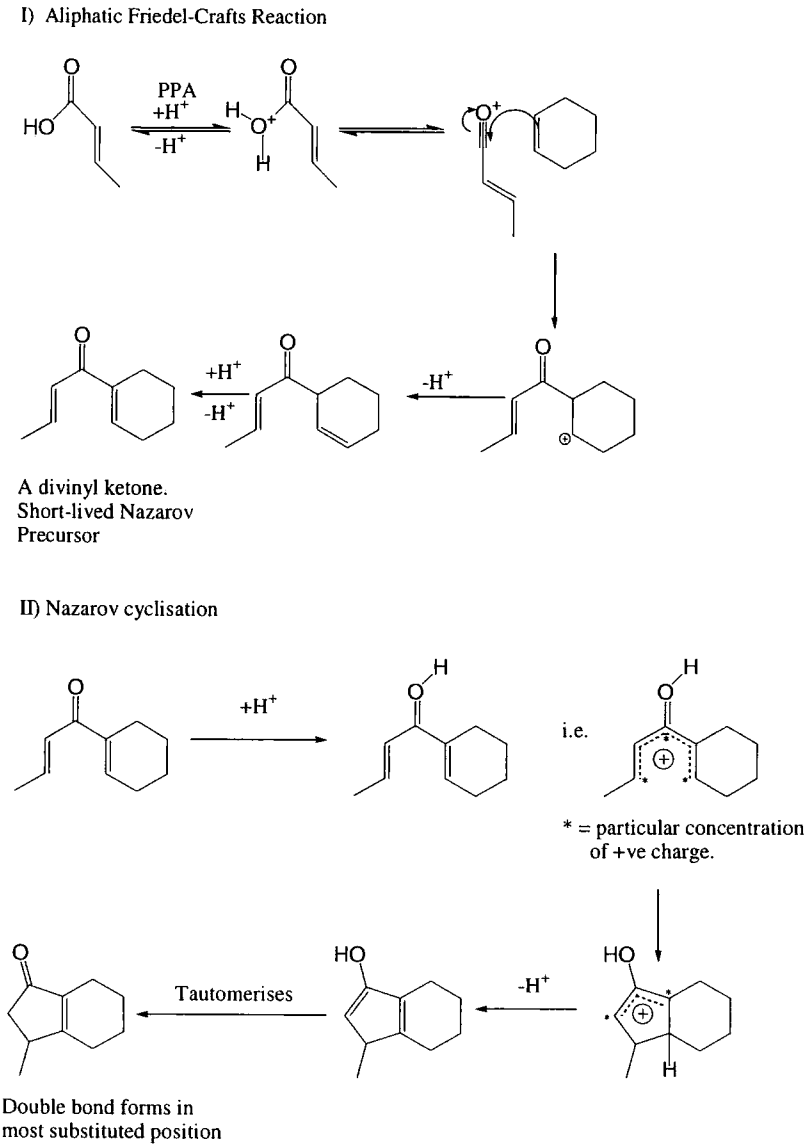
This section should be read in conjunction with Experiment 1 in the later section giving experimental details.

Crotonic acid (E-$CH_3CH{=}CHCO_2H$)and cyclohexene were reacted together in hot polyphosphoric acid* (PPA, see appendix 2) by a modified literature method.[3] Under these conditions, the powerfully dehydrating PPA removes an –OH unit from the crotonic acid, probably after initial protonation. The reactive acyllium cation formed takes part in an aliphatic Friedel-Crafts reaction with the cyclohexene[5] and the intermediate formed undergoes a Nazarov pericyclic conrotatory electrocyclisation.[6 - 8]

Detailed information on the aliphatic Friedel-Crafts and Nazarov reactions may be found in section 2.2.6 and the subsections thereof.

* Polyphosphoric acid, PPA. The abbreviation PPA' is used to denote polyphosphoric acid of standard concentration, i.e. 83% P_2O_5 by mass. For more information, see appendix 2.

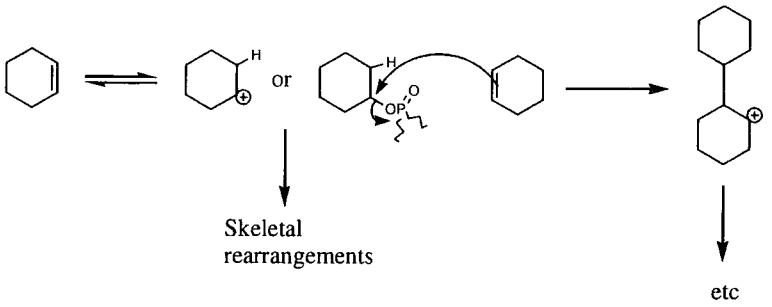
Figure 10. The aliphatic Friedel-Crafts Nazarov reaction between crotonic acid and cyclohexene in PPA



The aliphatic Friedel-Crafts reaction has been reviewed [5] as has the Nazarov cyclisation[6, 7, 9] (also see ref. 10).

The reaction gave a relatively low yield, a typical feature of the Nazarov reaction, and many byproducts including nasty tarry materials. It was noted that brown and black materials could be produced from cyclohexene and PPA' in the absence of crotonic acid and it is likely that cationic polymerisation was involved in this, see Figure 11.

Figure 11. Possible cationic polymerisation of cyclohexene



The author hypothesised that one factor contributing to the low yields of the Nazarov reaction might be found in the work-up. The literature work-up method involved using a small amount of NaOH solution to 'break up' the PPA,[3] but the mixture remaining after such treatment was still mostly phosphoric acid, only a very small proportion of it having been neutralised (P:Na ratio in product ~ 10:1). It is possible that an appreciable (although certainly not large) amount of the ketone product may remain dissolved in the acidic layer in a protonated (acyllium ion) form. Although this hypothesis was not deemed to be sufficiently important to be investigated in great detail, an alternative work-up using a much larger quantity of NaOH was tried. In a preparation involving 400g standard strength PPA', 184g NaOH was used for neutralisation, this being the quantity necessary to convert the phosphoric acid entirely to the very much less acidic NaH_2PO_4.

The yield obtained (46%) was better than for earlier attempts using methods close to the literature method, but was lower than the yield quoted in the literature (55%).[3] However, there were too many variables in the experiment to allow the value of the yield to be given great significance.

One final note on the yield of HK1: It may be that the yield can be improved by using cyclohexyl crotonate as starting material rather than cyclohexene and crotonic acid. There are cases in the literature where the use of esters gives a better yield than is obtained from a carboxylic acid and alkene.[11]

3.3.2.2 Experiment to test for possible gases evolved during the reaction between PPA, crotonic acid and cyclohexene

During several syntheses of HK1, the level of foaming in the reaction flask seemed to be greater than could be explained by refluxing of the cyclohexene under the heat of reaction. Additionally, the volume of gas passing out of the condenser, sometimes in a stream fast enough to carry cyclohexene vapour through, appeared to be much bigger than could be accounted for by thermal expansion of the air within the ~4l flask and, more importantly, displacement of the

air by cyclohexene vapour. It was therefore hypothesised that decomposition reactions might have been producing a stream of ethylene and/or other volatile materials. To test this idea, an HK1 synthesis (~0.7 mol scale) was run in apparatus designed to intercept any condensable gases. The only outlet for gases from the reaction flask was through a worm-tube condenser, cooled by tap water to intercept cyclohexene vapour, then through a trap cooled by liquid nitrogen and out through a bubbler.

The result of the above experiment was that nothing apart from a slight mist of cyclohexene condensed in the liquid nitrogen cooled trap. Additionally, the rate of gas flow through the bubbler did not appear to be above what would be expected from a couple of litres of nitrogen displaced by cyclohexene vapour, although detailed quantitative measurements were not made (and would not have been very useful anyway as some gas escaped through the worn and defective stirrer shaft seal). The intuitive feeling from the earlier observations of foaming rate and rate of gas flow through the condenser was that substantial volumes of gas were being evolved, but this experiment showed that the intuition was wrong and that little or no gas was evolved.*

3.3.2.3 Cyclohexyl crotonate contamination of HK1

Analysis of samples of HK1 from early syntheses by gas chromatography gave two peaks with an area ratio of roughly 4:5 (lower retention time:higher retention time). The higher peak was shown to be the required compound and the other peak was shown to be cyclohexyl crotonate by a final year student.[12] Production of esters under the reaction conditions used has been previously documented.[13 - 15] In the case of the synthesis in this current project, it did not prove necessary to separate the HK1 from the ester. The presence of the latter had two minor implications- a) The yield of HK1 was actually not much more than half the apparent yield and b), The apparent yields in subsequent reactions utilising crude HK1 as a starting material were depressed.

3.3.2.4 Improving the synthesis of HK1 and producing a purer product

During the course of the experimental work, HK1 was synthesised a total of eight times. Variations were made to each synthesis to see if the yield, and more particularly, ease of work-

* CO and CH_4 would probably not have been condensed if they were much diluted by N_2, and H_2 would definitely not be condensed. Evolution of these gases cannot be ruled out, but any volumes evolved would probably be insignificant.

up on a large scale could be improved. Experiments were also carried out with the aim of preparing a purer product.

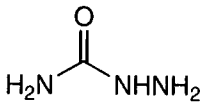
With regard to the purification of crude HK1, simple vacuum distillation, the method employed in the literature preparations,[2, 3] could not be made to give a product completely free of cyclohexyl crotonate impurity. Distillation with a short (15cm) vigreaux column was little better. The ester was marginally more volatile than the ketone but the difference was insufficient to allow for a clean separation. (Also refer to the distillation step in Experiment 2.) The two may have been completely separable by well controlled fractional distillation with continual monitoring of the distillate to determine the changeover point.* However, such a distillation would probably have to employ a large reflux ratio (i.e. a high proportion of the vapour emanating from the boiler would be condensed at the top of the fractionating column, the liquid running back down through the column) and would thus be rather slow as the liquid would, effectively, have to be reboiled many times. This might cause a reduction in yield due to decomposition in the boiler. There would also be waste due to hold-up in the column and in the ketone/ester mixture which would be collected around the changeover point, so a chemical purification procedure involving semicarbazide was developed as an efficient alternative.

It is relevant to note that a final year student looked into the problem and tried to remove cyclohexyl crotonate from crude HK1 by saponifying it with aqueous sodium hydroxide, but the yields were low.[12] The student also tried to avoid the production of cyclohexyl crotonate in the first place by using longer reaction times in the initial synthesis, the rationale being that cyclohexyl crotonate is converted to HK1 by PPA. Unfortunately, this also proved to be an unsatisfactory technique as the longer reaction times gave a very low yield of HK1 (although the ester content was quite low) and a large quantity of tar was formed.

* Instead of continual monitoring, lots of small fractions could have been obtained. Neither method would have been practical with the equipment to hand. The adaptors available for vacuum distillation allowed for a maximum of four separate receptacles for distillate. With regard to continuous monitoring, the boiling points were too close for any sudden temperature rise to be discernable around the changeover (with the simple distillation which was employed) and IR or other methods would have involved rushing back and forth to use equipment in different parts of the building.

3.3.2.5 Use of semicarbazide to prepare pure HK1

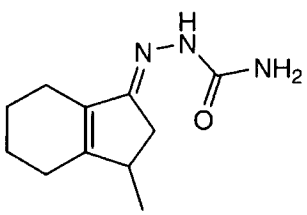
Figure 12. Semicarbazide



Semicarbazide, $H_2NN(H)C(O)NH_2$, is one of several strongly nucleophilic $R(R')XNH_2$* reagents which easily react with ketones to form conveniently crystalline derivatives. The presence of the electronegative substituent X gives these reagents a higher nucleophillicity than simple amines due to the so called *α effect.*† The R(R')XN=CR"R"' compounds produced by reaction with ketones are much more resistant to hydrolysis than imines or aminals. Besides semicarbazide, other common $R(R')XNH_2$ reagents are hydroxylamine, phenylhydrazine and 2,4-dinitrophenylhydrazine, but semicarbazide gives the most easily hydrolysed derivatives so it was chosen for trial.

It was found that a solution of semicarbazide hydrochloride (semiHCl) buffered by NaOAc in a water/ethanol mixture easily reacted with HK1 to produce a highly insoluble and crystalline semicarbazone, known as HK1semicarbazone. The reaction could simply be run by leaving the mixture in the dark at room temperature for a couple of days, or it could be left for 3 – 4 hours at 50 – 55°C. Recovered yields of the crystals were at least 92%.

Figure 13. HK1semicarbazone



Hydrolysis of the semicarbazone of HK1 was easily accomplished by vigorously stirring with a mixture of dilute aqueous HCl and cyclohexane at 85°C for 90 mins. Recovered yields of washed and dried HK1 were typically 96% based on the mass of HK1semicarbazone (88%based on the ketone content of the crude ketone used to make the semicarbazone). The purity of the HK1 obtained from the hydrolysis of the semicarbazone was roughly estimated to be at least

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* X = O or N; R, R' = organic groups and/or H; R' is absent when X = O

† This effect is imperfectly understood and is interesting because of it's counterintuitive nature. It might be expected that the electron withdrawing effect of the electronegative X group would make the lone pair on NH_2 less available and thus reduce nucleophillicity, but nuclephillicity is actually enhanced by X. See *Advanced Organic Chemistry*, 4th Edition, J. March, (1992), Wiley, Chichester.

98% by GC-FID and the cyclohexyl crotonate content varied between miniscule and undetectable.

3.3.2.6 NMR investigations of pure HK1

Note: All chemical shifts are referenced to tetramethylsilane, the ^{1}H and ^{13}C chemical shifts of which are defined as being at 0ppm in any specified solvent.

The availability of pure HK1 prepared by the use of semicarbazide allowed an in-depth NMR investigation to be run. The object was to try and assign all of the peaks in the NMR spectrum. Although this was not achieved, many of the more important lines were assigned unambiguously. To begin with, ^{13}C and ^{1}H spectra were run on high frequency machines. The results were as follows:

^{1}H NMR results, $CDCl_3$ solvent, TMS reference, 500MHz				
δ/ppm	Multiplicity	J/Hz	Number of H (from integration)	Comments
1.16	d	6.70	3	
1.55-1.63	complex m	not clear	1	These two sets of peaks were partially merged together.
1.63-1.80	complex m	not clear	3	
1.91	d of d	18.49 and 1.50	1	
2.09	m	2.00 (average)	2	> 6 improperly resolved peaks
2.20 (average)	d of t	5.00 and 20.00	1	"points" slightly towards peak at 2.43ppm
2.43 (average)	d of t	6.50 and 19.50	1	"points" slightly towards peak at 2.20ppm
2.58	d of d	6.50 and 18.49	1	
2.76	m	not clear	1	Poorly resolved

^{13}C NMR results, $CDCl_3$ solvent, TMS reference, 125.7MHz	**DEPT results, $CDCl_3$ solvent, TMS reference** ^{13}C 100.6MHz, ^{1}H decoupled 400MHz
δ/ppm	DEPT assignment
18.8	CH_3
20.0	CH_2
21.7	CH_2
22.3	CH_2
25.9	CH_2
36.3	CH
43.5	CH_2
137.8	C
177.0	C
207.4	C

3.3.2.6.1 Interpretation of the NMR spectra of HK1

^{1}H COSY and ^{1}H-^{13}C HMQC spectra were also obtained and will be referred to in the analysis which now follows. The analysis is here written in the order in which it was performed so as to make it as easy as possible to follow the underlying thinking and logic.

Figure 14. An arbitrary system of numbering the carbon atoms in HK1, as used in the present NMR analysis.

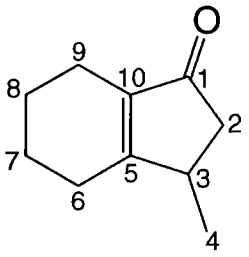
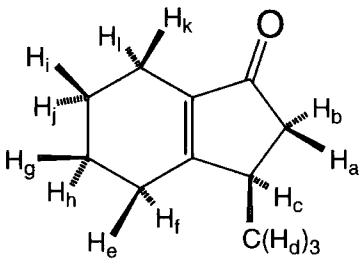


Figure 15. A system of lettering to denote the various hydrogen positions



Predicted chemical shifts were obtained using the empirical rules given in ref. 16. A further set of predictions were also made using the *estimate* function on SpecInfo3.2, a spectrum prediction and assignment computer program available via ftp from the UK national laboratories at Daresbury.* All estimated coupling constants were calculated using the empirical rules given in ref. 16.

* SpecInfo3.2 is able to provide estimated ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR chemical shifts for a molecule whose structure is drawn in the formula editor window. There are two different chemical shift estimating functions which can be selected; the *predict* and the *estimate* functions. The *estimate* function calculates chemical shifts one atom at a time by applying empirical rules to approximate the influence on chemical shift of the type of bonding (single, double, triple, allylic, aromatic) and of the influence of other nuclei in α, β, γ, etc positions. The *predict* function trawls through the large databases of structures and spectra available to SpecInfo3.2 to find the chemical shifts of atoms with similar connectivities to those in the molecule entered; the values obtained are presumably automatically averaged in some way to provide the final predicted chemical shifts. For the purposes of the current work, the *estimate* rather than the *predict* function was used as it seemed to commonly provide slightly better results.

Estimated ^{1}H chemical shifts /ppm		
Position of atom	Value estimated using rules in ref. 16	Value estimated using *estimate* function in SpecInfo3.2
H_a	2.7	2.94
H_b	2.7	2.94
H_c	2.6	2.57
H_d	1.1	1.16
H_e	2.05	1.96
H_f	2.05	1.96
H_g	~ 1.7	1.65
H_h	~ 1.7	1.65
H_i	~ 1.7	1.65
H_j	~ 1.7	1.65
H_k	2.25	1.96
H_l	2.25	1.96

A simple ball and stick model showed that H_c and H_b would be approximately eclipsed while there would be an approximately 120° dihedral angle between H_c and H_a. Using the Karplus equation[16] with the standard values of J^0=8.5Hz and J^{180}=9.5Hz gave the following estimates: $J(H_cH_b)$=8Hz and $J(H_aH_c)$=2Hz.

We are now in a position to assign some of the ^1H resonances:

Initial ^1H assignments		
Chemical shift of peak from actual ^1H spectrum /ppm Coupling constants /Hz (where measurable)	Assignment and corresponding estimated chemical shift (rounded off) /ppm	Reasoning and comments
1.16 6.70Hz	H_d, 1.1-1.2	Identified by integral (showing 3H), chemical shift and multiplicity (d, J = 6.70Hz, a typical $^3J_{(CH)}$ coupling constant). Unambiguous and the obvious first resonance to assign.
2.76 ?Hz (poorly resolved m)	H_c, 2.6	Consistent with integral and estimated chemical shift. Importantly, COSY shows coupling to H_d (1.16ppm). This allows definite identification of H_c as H_d does not appreciably couple to anything else.
1.91 18.49Hz and 1.50Hz	H_a, 2.7-2.9	H_a and H_b were unambiguously assigned using coupling information from the ^1H spectrum and confirmed by the COSY. (The estimated chemical shift values were not helpful and mainly served to illustrate the deficiencies in the estimation algorithms when applied to ^1H in the vicinity of double bonds, electronegative groups, etc.) From the ^1H spectrum, $J_{(HaHb)}$= 18.49Hz. This is consistent with geminal coupling between H atoms which are hyperconjugated with a carbonyl double bond (ref. 16, p 97). The high value indicates very favourable hyperconjugation; the C=C bond could also play a role. The COSY spectrum showed H_a and H_b, both coupling to H_c. One couples more strongly than the other, and from the ^1H spectrum the coupling constants were measured as 1.50Hz and 6.50Hz. J values estimated using the Karplus equation (see last paragraph on previous page) allow the H_a and H_b resonances to be differentiated and assigned. The estimated values are $J(H_aH_c)$=2Hz and $J(H_bH_c)$=8Hz. From this it is clear that the 1.91ppm resonance with J=1.50Hz belongs to H_a and the 2.58ppm, J=6.50Hz resonance is associated with H_b.
2.58 18.49Hz and 6.50Hz	H_b, 2.7-2.9	

Estimated ^{13}C chemical shifts /ppm		
Position of atom	Value estimated using rules in ref. 16 (Conformational corrections were ignored)	Value estimated using *estimate* function in SpecInfo3.2
C1	>198*	207.6
C2	39.5	43.6
C3	33	36.3
C4	15.4	18.8
C5	150.8	177.0
C6	37.9	22.4
C7	Not calculated	20.1
C8	Not calculated	22.1
C9	34.7	26.0
C10	128	137.9

Simply from estimated ^{13}C chemical shifts, three of the resonances can be assigned with a high level of confidence:

Initial ^{13}C assignments:		
Measured chemical shift /ppm	Assignment	Estimated chemical shifts /ppm (Also see table above)
207.4	C1	>198-207.6
177.0	C5	150.8-177.0
137.8	C10	128.1-137.9

It can be seen that the use of SpecInfo3.3 for the estimation of ^{13}C chemical shifts seems to give values close to those measured, at least for highly deshielded carbons.

HMQC results:

The HMQC spectrometer was very sensitive and revealed a multitude of 1, 2 and 3 bond ^{1}H-^{13}C couplings.

From the HMQC spectrum, C1 was seen to couple strongly to H_a and H_b, with further very weak coupling to several more H including H_c.

C5 and C10 both coupled strongly to many H with the following relationships being particularly notable:

C5 couples to H_c more strongly than does C10 (as would be predicted).

C5 couples to both H_a and H_b more strongly than does C10 (interesting).

C5 couples strongly with H_d, but H_d does not couple with C1 or C10 (as would be predicted, and a useful confirmation of the correctness of the C5 and C10 assignments).

* The carbonyl carbon in cyclohex-2-en-1-one resonates at 198ppm relative to TMS.

Further ^{13}C assignments:

Several other carbon resonances could be assigned, although not with much confidence in some cases.

Further ^{13}C assignments, some very tentative			
Measured chemical shift /ppm and hydrogen connectivity from DEPT	Assignment	Estimated chemical shifts (values from SpecInfo3.3) /ppm (Also see table above)	HMQC information and comments
18.8, CH_3	C4	18.8	Clearly the correct assignment from chemical shift and DEPT. However, C4 ought to couple strongly to H_d, but the HMQC spectrum did not show this clearly.
36.3, CH	C3	36.3	Unambiguous on chemical shift and DEPT grounds.
43.5, CH_2	C2	43.6	Unambiguous on chemical shift grounds. Clearly the highest frequency methylene carbon resonance. But the HMQC spectrum seemed to show no coupling to H_a and H_b. This is very curious and is not yet explicable.
25.9, CH_2	C9	26.0	Assigned mainly on chemical shift. HMQC shows weak coupling to H_b, no coupling to H_a and H_c. There is strong coupling to the complex 4H system between 1.55 and 1.8ppm, as would be expected (these H are probably on C7 and C8).
20.0	C7	20.1 (20.05 before rounding)	Very provisional assignment.

3.3.2.6.2 Conclusions from NMR investigation of HK1.

The HMQC spectrum showed some anomalies which may be artifacts. A re-running of the spectrum, preferably at a slightly lower level of sensitivity, may be useful.

The assignments which could be made with certainty, even without much input from the possibly unreliable HMQC information, were entirely consistent with the proposed molecular formula. In particular, the H_a, H_b, H_c, $3H_d$ system of resonances and couplings and the number of quaternary and tertiary carbons as counted by the DEPT together provided sufficient

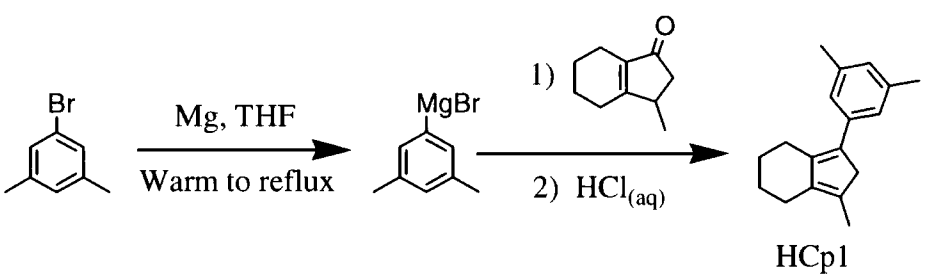
information to absolutely rule out any double-bond isomers other than the one proposed. (The detailed argument has not been explicitly shown as it is quite trivial to visualise other double bond isomers and see that they would be highly incompatible with the spectral information).

It is interesting to note that the double bond isomer of HK1 indicated by NMR is the one which would be expected on chemical grounds. Easy migration of C=C bonds under the vigorously acidic Nazarov conditions gives the thermodynamically favoured isomer. In the case of HK1, the isomer which NMR shows to be produced is the only possible one containing a double bond which is both tetrasubstituted and conjugated with the carbonyl group.

3.3.3 Synthesis of 1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene (HCp1)

Attempts were made to prepare a Grignard solution from 1-bromo-3,5-dimethylbenzene using Et_2O as the solvent but success was not achieved. THF was tried in conjunction with 1,2-dibromoethane as an 'entrainer' (see methods discussed in refs. 17 - 19); this was successful but it was afterwards found that THF alone was entirely satisfactory. Reaction of HK1 with the Grignard presumably gave an alkoxide which hydrolysed, then eliminated water on workup to give 1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene, HCp1. The reaction is outlined in Figure 16.

Figure 16. The preparation of 1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene, HCp1

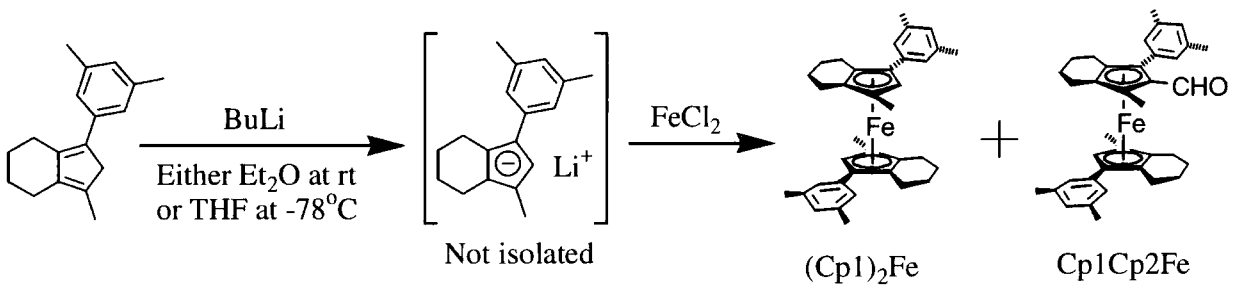


3.3.4 Synthesis of substituted ferrocenes

It was found that HCp1 was easily deprotonated by BuLi in THF or Et_2O. The deprotonated material was reacted with anhydrous $FeCl_2$ and the product subjected to column chromatography, as outlined in Figure 17. Three substances were isolated; an orange compound, a red compound and a very small quantity of a green substance produced by decomposition on the column. C,H,N analysis and mass spectral information indicated that the orange compound was the ferrocene *bis*{η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]}iron(II), also known as $(Cp1)_2Fe$. The ^1H spectrum showed a peak at

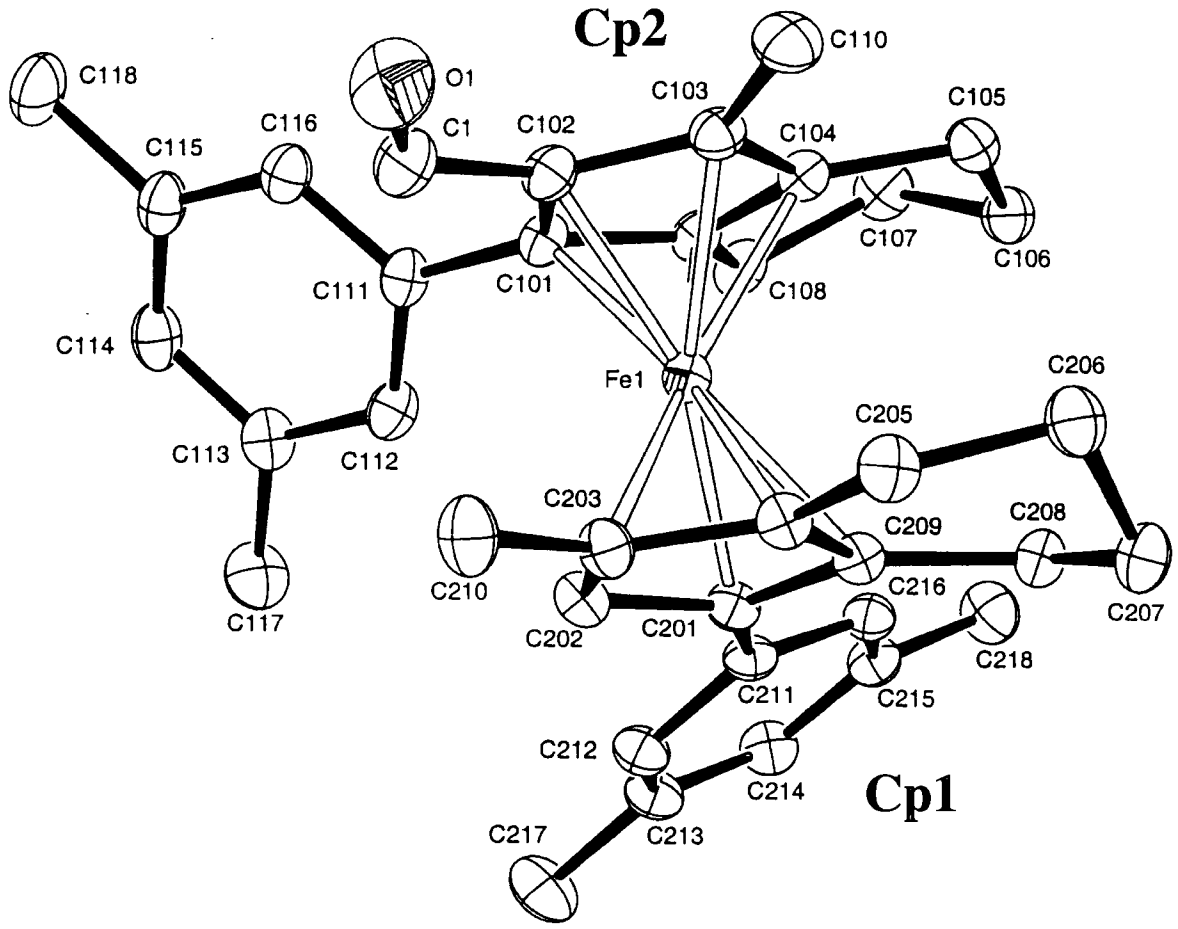
3.72 ppm (s, 1H), characteristic of a ferrocene Cp-H. The analogous ferrocene *meso-bis*(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl)iron(II), previously prepared at Durham, had a corresponding peak at 3.79 ppm.[2]

Figure 17. The preparation of a mixture of $(Cp1)_2Fe$ (*bis*{η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]}iron(II)) and Cp1Cp2Fe (η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]-η^5-[1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II))



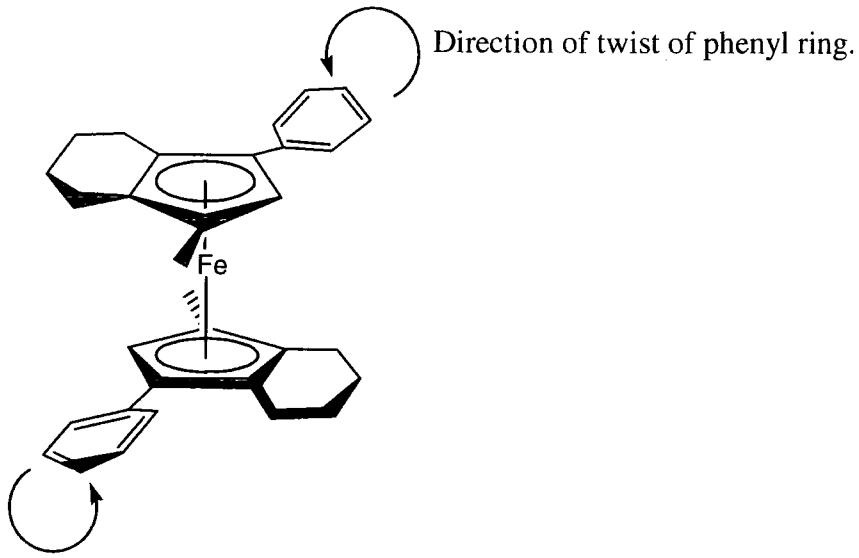
The red compound was only produced in extremely small quantities and NMR spectroscopy did not establish any useful data relating to it. In an attempt at finding a molecular formula, high-resolution mass spectroscopy was applied but the results turned out to be in error. The measured molecular mass was 558.266244 Da which did not correspond with any possible molecular formula to within an acceptable error (see section 3.5.6.2). Eventually, a small crystal was grown and used for an X-ray diffraction structural analysis; it turned out that the material was a formyl derivative of $(Cp1)_2Fe$, *viz* η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]-η^5-[1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II) ($C_{37}H_{42}FeO$, abbreviation Cp1Cp2Fe). The compound showed a pseudomeso arrangement of ligands, although since both ligands in each molecule were prochiral, but not identical, the molecules were dissymmetric. Unsurprisingly, the substance was produced in a racemic form. Insufficient material was obtained to determine if it was entirely composed of the pseudomeso isomer or whether there were two isomers which crystallised separately.

Figure 18. Cp1Cp2Fe (η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]-η^5-[1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II))



It is interesting to compare the solid-state molecular structure of Cp1Cp2Fe (Figure 18) with the structure of the related compound *meso-bis*(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl)iron(II), abbreviated to as $(Cp3)_2Fe$ (Figure 19).[2]

Figure 19. $(Cp3)_2Fe$ (*meso-bis*(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl)iron(II))



In the solid state, $(Cp3)_2Fe$ possesses a centrosymmetric structure in which the carbon atoms of the Cp rings are staggered and the bulky substituents are as remote from each other as possible, thus minimising steric hindrance.[2] The phenyl rings in $(Cp3)_2Fe$ are not coplanar with the Cp units, but twisted out of the mean Cp plane by 17.9° in the direction illustrated in Figure 19.* If the phenyl substituents were coplanar with the Cp rings then conjugation between the Cp and Ph π-bonding p orbitals would be at a maximum, but it appears that steric factors prevent this conformation from being achieved The Cp and Ph rings exhibit small distortions and the Cp-Ph bonds are directed such that the Ph point slightly away from the iron, but these factors are relatively minor.

Cp1Cp2Fe, containing two different ligands obviously has no centrosymmetric configuration, but it could adopt an analogous structure in which the bulky cyclohexyl and xylyl groups are as remote from each other as possible. This does not happen, the cyclohexyl group on the Cp2 ligand slightly overlapping both the cyclohexyl and xylyl groups on ligand Cp1, but the conformation overall is probably close to the least hindered possible.

It is hypothesised that the CHO group is an important factor in determining the molecular conformation of Cp1Cp2Fe. The CO unit is not far from being coplanar with the Cp ring (O1-C1-C102-C103 torsion angle = 14.7°), probably to maximise π conjugation between the two. Steric hindrance from both the CHO (which would be much less important if the CHO group were free to rotate out of the Cp plane) and cyclohexyl group forces the xylyl group of ligand Cp2 to twist substantially (mean of C102-C101-C111-C116 and C109-C101-C111-C112 torsion

* 17.9° refers to the dihedral angle between the mean Cp and mean Ph planes.[2]

angles = 51.5°). This twist puts C112, C117 and their associated hydrogens in a position in which they are a major factor in controlling the orientation of ligand Cp1.

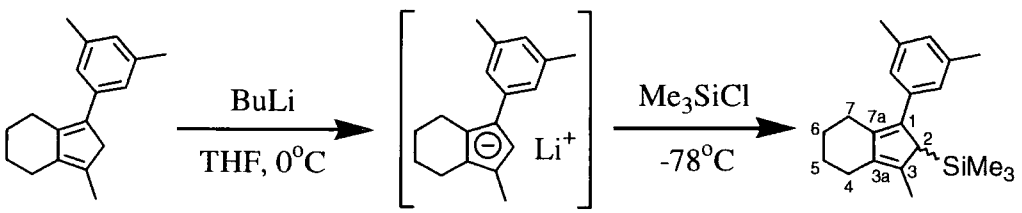
Ligand Cp1 is rotated around the Fe-Cp axis so as to minimise interactions between its methyl, cyclohexyl and xylyl units and C112/C117. The degree of rotation will also be influenced by the need to avoid too much overlap between its cyclohexyl and xylyl units and the cyclohexyl unit on ligand Cp2.

The xylyl group on ligand Cp1 is rotated substantially more than the phenyl rings in $(Cp3)_2Fe$ relative to the Cp groups (25° vs 17.9°)*. This rotation might be expected to give an unfavourable interaction between the C218 methyl group and the cyclohexyl unit on ligand Cp2, although hindrance between the ligand Cp1 xylyl and cyclohexyl groups would be reduced somewhat. However, the largest factor involved in promoting the twist may be the need to reduce interaction between the C117 and C217 methyl groups.

Although the qualitative arguments presented here to rationalise some of the interesting features of the solid-state molecular structure of Cp1Cp2Fe seem reasonable, they are rather speculative and more work involving space-filling models and quantitative computer calculations needs to be done.

3.3.5 Synthesis of (R,S)-1-(3,5-dimethylphenyl)-2-(trimethylsilyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene. (TMSCp1).

Figure 20. The preparation of (Trimethylsilyl)cyclopentadiene 1, TMSCp1 ((*R,S*)-1-(3,5-dimethylphenyl)-2-(trimethylsilyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene)



* 24.6° = mean of torsion angles C202-C201-C211-C212 and C209-C201-C211-C216 in Cp1Cp2Fe.

17.9° = dihedral angle between mean Cp plane and mean Ph plane in *bis*(1-phenyl-3-methyl-4,5,6,7-tetrahydroindenyl)iron(II).[2]

Since the Cp and xylyl rings in the Cp1 unit of Cp1Cp2Fe are not greatly distorted, it is expected that a calculation of dihedral angle based on the mean Cp and xylyl planes would be tolerably close to 24.6°. For the purposes of the present qualitative discussion it is valid to compare the values 24.6° and 17.9° even though they refer to slightly different things. It would, however, be useful to calculate the angle for Cp1Cp2Fe based on mean planes.

(R,S)-1-(3,5-dimethylphenyl)-2-(trimethylsilyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene. (TMSCp1) was prepared by the reaction of deprotonated HCp1 with trimethylsilyl chloride (Figure 20). The material turned out to be a crystalline solid which could be stored safely in air for up to two weeks. (After approximately six weeks in air it decomposed to give a treacle-like mixture which was not analysed.) The unremarkable structure was determined by X-ray diffraction and is shown in Appendix 3.

3.3.6 The reaction of TMSCp1 with early transition metal chlorides

As discussed in the literature review section of this thesis, the reaction of trimethylsilylcyclopentadienes with transition metal chlorides is an excellent method for the synthesis of monocyclopentadienyl complexes.* Not only is the reaction facile, but the byproduct, Me_3SiCl, is volatile and easily removed under vacuum.

The reaction of TMSCp1 with several metal chlorides was examined. Interaction of TMSCp1 with $ZrCl_4$ at room temperature in various solvents gave an uncrystallisable, not very soluble amorphous brown mass. No pure substances could be extracted using a variety of solvents and recrystalisation was futile. As a result, no useful analytical results could be obtained. The reaction of TMSCp1 with $NbCl_5$ gave similarly frustrating results with a black tarry material being formed.

Reaction of TMSCp1 with $TiCl_4$ in mixed hexanes gave a red crystalline material as the major product whereas the same reaction in dichloromethane appeared to give an insoluble brown material, although this was later discovered to be due to a slight contamination of the dichloromethane by water. The red compound was very highly soluble in dichloromethane and of moderate solubility in mixed hexanes. The difference in solubilities enabled the compound to be recrystalised using the solvent diffusion technique. A very concentrated solution of the material in CH_2Cl_2 was prepared by evaporation of a more dilute solution,† then a thick layer of mixed hexanes was floated on top.‡ Crystals formed as the solvents diffused into each other, but unfortunately the crystals consisted of badly formed long thin plates, not at all suitable for X-ray investigation.

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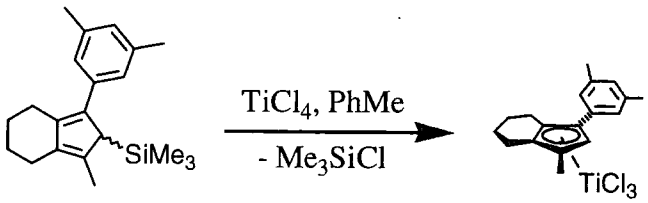
* Analagous reactions also occur with diethylaluminium or trimethyltin substituted cyclopentadienes.

† It was found easier to prepare a very concentrated solution by evaporation rather than the more fiddly technique of trying to dissolve the solid in a tiny volume of CH_2Cl_2. The latter method was also slow as the last traces of solid would take a prolonged time to dissolve. The solutions prepared were as close to saturation at room temperature as could be managed

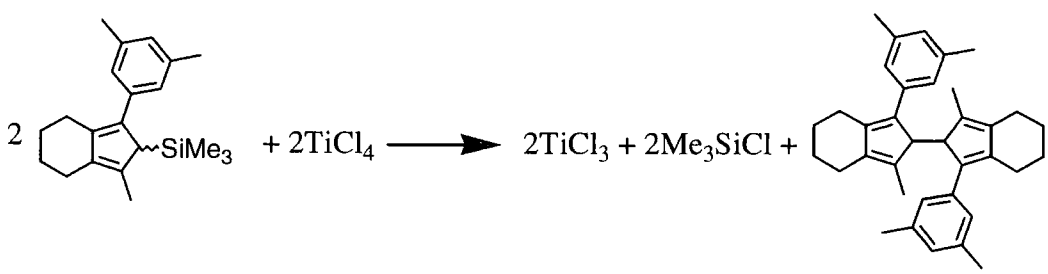
‡ For example, a 0.5cm layer of nearly saturated CH_2Cl_2 solution would have a layer of approximately 4cm mixed hexanes floated on top.

Figure 21. The preparation of Cp1TiCl$_3$ (η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]trichlorotitanium(IV))



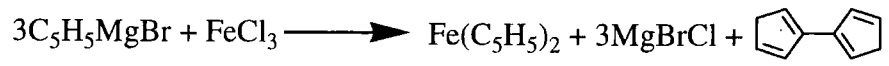
Mass spectroscopy of the red compound showed two equally intense peaks with m/z = 390 and 392, plus several smaller additional peaks. The m/z values and relative intensities were correct for the isotope distribution for $C_{18}H_{21}TiCl_3^+$, i.e. the molecular ion of the expected compound η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]trichlorotitanium(IV). Interestingly, there was also a peak at m/z = 474, showing an isotope ratio typical of a C,H compound. This peak is provisionally ascribed to $C_{36}H_{42}^+$, i.e. dimerised ligand, presumably produced as an impurity by a redox process taking place during the reaction between $TiCl_4$ and TMSCp1 (Figure 22). Such redox reactions are common when oxidising transition metal chlorides react with reagents containing anionic cyclopentadienyl, this being a moderate reducing agent (Figure 23). Indeed, Ti(IV) cyclopentadienyl complexes are often made using a source of anionic cyclopentadienyl (e.g. a lithiated cyclopentadiene) and $TiCl_3$, with subsequent oxidation of the resulting complex to the required Ti(IV) state. This procedure avoids the oxidative dimerisation of the ligand which otherwise takes place as a side reaction even though the oxidising power of Ti(IV) is quite limited.

Figure 22. The proposed oxidative dimerisation of Cp1 during the reaction between TMSCp1 and $TiCl_4$



$(Cp1)_2$, dimerised ligand

Figure 23. The Oxidative Dimerisation of Cyclopentadienyl Anions By Iron(III) Chloride[20]



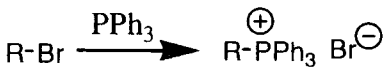
(A similar reaction takes place between chromium(III) chloride and sodium cyclopentadienide)

3.3.7 Speculative experimental work

A novel route to *ansa*-cyclopentadiene complexes based on the chemistry of phosphonium salts and phosphorous ylids was proposed and some initial experimental work started. Pressure of time caused the experimental work to be abandoned when it had barely extended past syntheses pre-existing in the literature; no data was accumulated. It is worth, however, setting out the proposed synthesis as another experimentalist may like to take up the challenge of investigating it from the beginning and trying to find conditions which will allow for a successful reaction, if possible. The synthesis was to be based around a number of known reactions which will now be laid out.

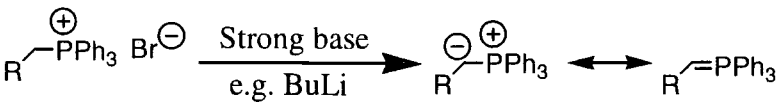
The facile reaction of triphenylphosphine with alkyl bromides is a straightforward and well known method of synthesising quaternary phosphonium bromides (Figure 24).

Figure 24. The formation of alkyltriphenylphophonium bromides



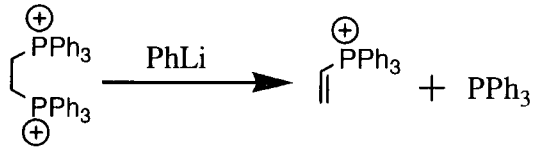
Phosphorus ylids, also known as Wittig reagents result from deprotonation of alkyltriphenylphosphonium bromides containing one or more α-hydrogen atoms as shown in Figure 25.

Figure 25. The formation of phosphorous ylids



Bis(phosphonium) salts and bis-ylids can be formed in a similar way to the monomeric analogues provided the phosphorus atoms are sufficiently well separated. 1,2-Bisphosphonium salts eliminate on deprotonation (Figure 26), although for bisphosphonium salts with phosphorus atoms separated by three or more carbon atoms, ylid formation is straightforward.[21]

Figure 26. The elimination reaction which occurs on deprotonating a 1,2-bisphosphonium salt



Phosphorus ylids can be alkylated using alkyl halides (Figure 27). The reaction can be extended into a method of synthesising rings as shown in Figure 28. Pyrolysis of phosphonium bromides results in elimination of HBr and PPh_3 and in the production of an alkene, illustrated in Figure 29.

Figure 27. Alkylation of phosphorus ylids

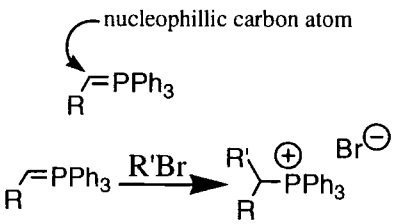


Figure 28. Formation of carbocycles by intermolecular-intramolecular double alkylation of a phosphorus ylid.

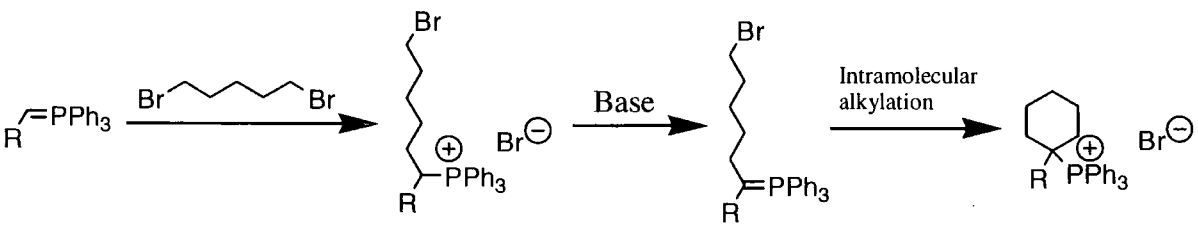
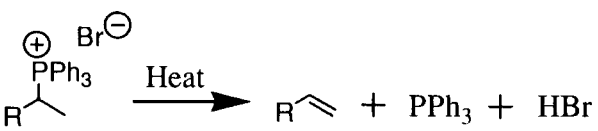


Figure 29. Pyrolysis of phosphonium salts



It was proposed to combine the above known reactions into a new *ansa*-cyclopentadiene synthesis along the lines of the scheme shown in Figure 30. It was expected that there would be difficulties in the procedure, in particular in the final cyclisation. Although saturated alicycles can be synthesised by the use of dibromides and phosphorus ylids (Figure 28), no references could be found for the use of unsaturated dibromides such as *cis*-1,4-dibromobut-2-ene. The unsaturation could well throw up difficulties, for example in the selection of a base for the second deprotonation. It may well require a base of exceptionally low nucleophilicity (lower

than the common LDA) to avoid reaction with the reactive allylic bromine atoms. On the positive side, though, the allylic bromines would probably be readily displaced by nucleophillic attack of the ylid. If the use of an unsaturated dibromide proves to not work at all, then a saturated dibromide substituted with a group inert to the reaction conditions, but with the potential to be converted to a C=C double bond at a later stage, could be employed. Alternatively, a dibromide of the form shown in Figure 31 could be utilised. Such a dibromide would give a cyclopentene sporting an exocyclic double bond in the first instance, but the bond could be isomerised into the ring as a last step to give the cyclopentadiene.

Although it possible that the ylid route would be able to access *ansa*-ligands, as illustrated in Figure 30, this is ambitious and monocyclopentadienes may be a more realistic target.

Figure 30. A proposed scheme for the synthesis of cyclopentadienes

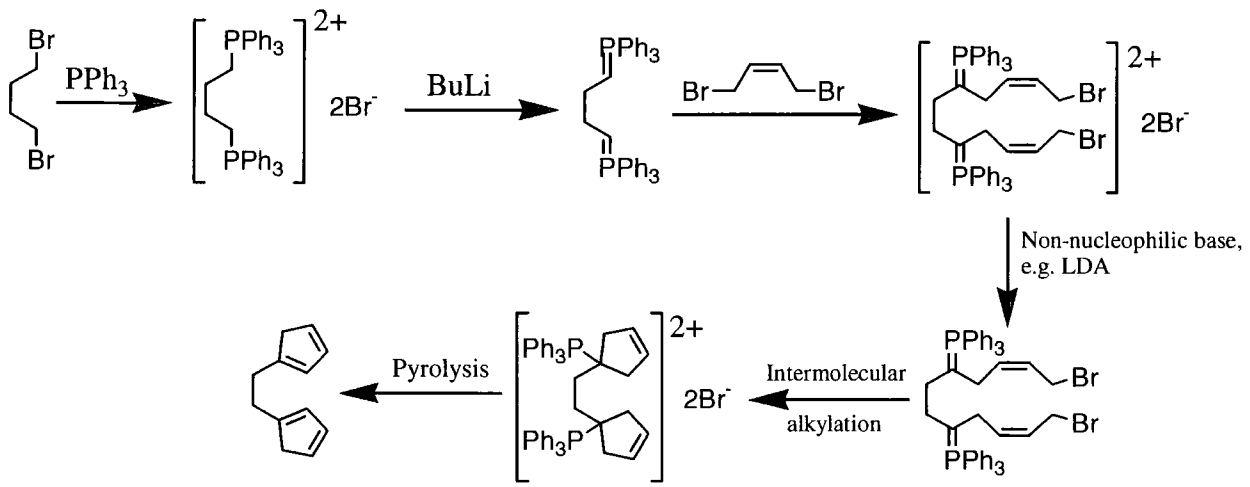
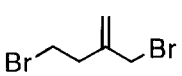
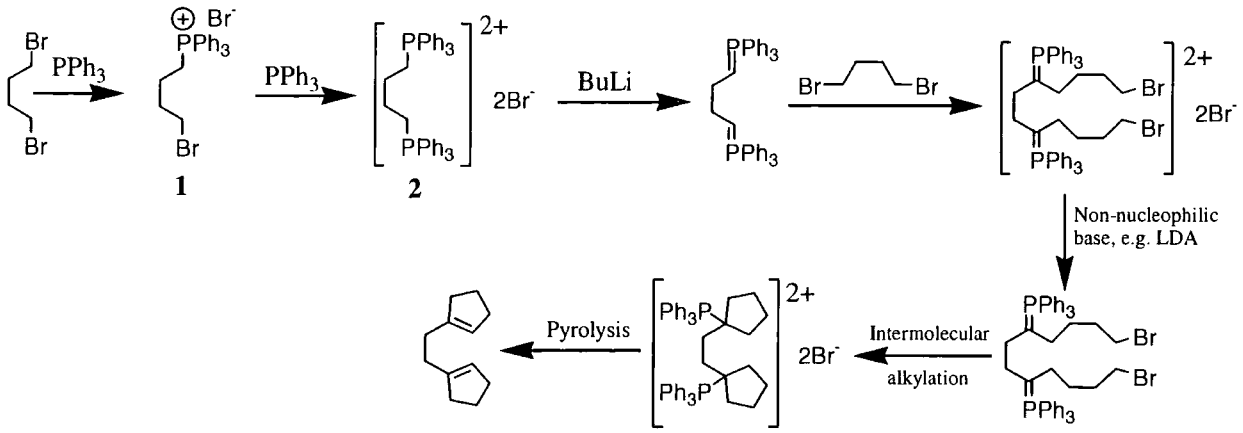


Figure 31. 2-Bromomethyl-4-bromobut-1-ene



The experimental work which was actually carried out aimed to reproduce the scheme in Figure 30, but using 1,4-dibromobutane instead of *cis*-1,4-dibromobut-2-ene so as to be closer to known reactions. Figure 32 outlines the intended procedure. Compounds **1** and **2** were prepared from 1,4-dibromobutane and triphenylphosphine by literature methods[22], but the investigation then had to be dropped due to various external factors. It is hoped that some future chemist will be tempted to resume work in this area.

Figure 32. A reaction sequence of which the first two steps only were completed.



3.4 Conclusions

The aliphatic Friedel-Crafts/Nazarov reaction between crotonic acid and cyclohexene in warm polyphosphoric acid is an established method of synthesising 3-methyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-one (HK1). The technique has been improved by adding a semicarbazone formation-hydrolysis purification step to remove the inevitable cyclohexyl crotonate byproduct.

1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene (HCp1) can be easily prepared from 3-methyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-one (HK1) by the use of 3,5-dimethylphenyl magnesium bromide in THF. HCp1 is highly convenient on account of its crystallinity and can be used to make metal complexes either by deprotonation and reaction with a metal chloride ($FeCl_2$) or through prior conversion to (*R,S*)-1-(3,5-dimethylphenyl)-2-(trimethylsilyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene (TMSCp1). The latter compound readily reacts with $ZrCl_4$, $TiCl_4$ and $NbCl_5$, although only the reaction with $TiCl_4$ leads to a isolable compound, η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]trichlorotitanium(IV) (Cp1$TiCl_3$).

The reaction of deprotonated HCp1 with $FeCl_2$ produces two ferrocenes, a major product, *bis*-η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II) ((Cp1)$_2$Fe), and a minor product, η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]-η^5-[1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II) (Cp1Cp2Fe). The minor product is thought to derive from some unknown impurity in the starting materials.

Crystal structures of TMSCp1 and Cp1Cp2Fe have been obtained.

A novel organophosphorus route to cyclopentadienes was proposed but was not carried out. It has been presented (section 4.3.7) in the hope that another chemist will be inspired to investigate it's practicality.

3.5 Preparative procedures and characterisation data.

3.5.1 Experiment 1: Preparation of 3-methyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-one (HK1) by one of the earlier-tried procedures

PPA' (400g {equivalent to 68g H_2O + 332g (2.3 mol) P_2O_5}) was mechanically stirred in a large flask fitted with a worm-tube reflux condenser and pressure-equalising dropping funnel. The flask was kept at 60°C in a water bath. Crotonic acid (57.4 g, 0.667 mol) was added in one lot and stirred until it had completely dissolved (~2h). Cyclohexene (57.6 g, 0.701 mol) was run-in over a period of 30 min in several small lots, with vigorous stirring to incorporate it and prevent it from simply floating on the surface. The reaction was run with stirring for a further 1 ½ – 2 h (60 °C), then cooled in ice-water. Crushed ice (200 g) was added to the tarry mass in small lots, care being taken to avoid an excessive temperature rise. When the ice had become incorporated, a cold solution of 140 g NaOH in 300 ml of water was added, initially in very small portions with strong cooling to keep the temperature below 60 °C. (Note: Neutralisation of the acid to a 1:1 Na:P ratio (184 g NaOH) was not carried out at this stage to reduce the probability of crystalisation.) On leaving the mixture for 2 days, it cleanly separated into two layers, a viscous black organic layer on top and a syrupy light-brown aqueous layer underneath. (The separation was much better than when the neutralisation was not carried so far – in the latter case, a black organic tarry material remained floating in the acid layer and made separations very difficult.) The aqueous and organic layers were separated and to remove entrained aqueous material from the latter, 100 ml mixed hexanes and 100 ml water were added and the mixture was shaken and separated. The aqueous washings from the organic layer were combined with the main aqueous layer, 100 ml water was added to reduce the viscosity and the mixture extracted with two 100 ml portions of mixed hexanes. To finish the neutralisation, NaOH solution (50 g in 150 ml water) was added to the aqueous layer which was then extracted with 200 ml mixed hexanes. All the organic extracts were combined, washed twice (2 × 200 ml water) and freed of acidic materials by washing twice with ammonia solution (2 × (30 ml 35% NH_3 + 70 ml water)). (The ammonia extracted a bright yellow flocculent material.) The solution was washed with 100 ml water, dried with anhydrous magnesium sulphate and the mixed hexanes removed on a rotary evaporator. The liquid product was vacuum distilled and collected in three grease-free bulbs under a constant pressure of 0.18 mmHg. The distillate was collected as follows:

Fraction	Water bath temperature /°C	Vapour temperature /°C	Mass collected /g
1	66	55-56	0.54g
2	70	56-54 (gradually reduced as the evaporation rate became low)	41.5
3	~92	54-62	3.68
		Total mass	45.7

All three fractions were very similar in composition and were combined. Overall yield = 46%* (based on crotonic acid)

3.5.1.1 Data characterising HK1

Material purified by distillation (contains some cyclohexyl crotonate impurity):

Appearance: Slightly viscous clear liquid

GC: 2 major peaks and several minor peaks. Relative areas of major peaks; 49386 (higher retention time, pure HK1) and 38390 (lower retention time, cyclohexyl crotonate).

GC-MS (EI) *m/z, rel.intens. /%*: HK1 fraction; 150 (M^+). Cyclohexyl crotonate fraction; no M^+; 99, 10% ($C_6H_{11}O^+$ or $C_6H_{10}OH^+$); 87, 80%; 69, 100% ($CH_3CHCHCO^+$ or $^+CH_2CHCHCHO$); 41, 40% (C_3H_5, allyl cation).

IR (Liquid film) /cm^{-1}: 1619 (sh), 1647 (vs), 1692 (vs) (CO str).

^{1}H-NMR δ /ppm ($CDCl_3$):6.9 (m), 5.8 (s), 5.7 (s), 1.1 (d), 0.8-2.8 (complicated m).

Material purified by the use of semicarbazide (free of cyclohexyl crotonate) (Also see sections 3.3.2.5 and 3.5.3):

GC-MS (EI) *m/z, rel. intens. /%*: 151, 10% (M^+ isotope peak); 150, 84% (M^+); 149, 14% (M^+-H^+); 135, 100% (M^+- $CH_3^\bullet$); 136, 11% (M^+- $CH_3^\bullet$ isotope peak); 122, 24% (-CO); 107, 47% (-$CH_3^\bullet$, -CO); 79, 87% (?); (Relative intensities rounded off to nearest 1%)

See section 3.3.2.6 for ^{1}H and ^{13}C NMR information.

3.5.2 Experiment 2: The fifth HK1 synthesis

80g (0.93 mol) Crotonic acid was stirred mechanically into 500g PPA' in a reaction flask fitted with an efficient water cooled worm tube reflux condenser and heated to 60°C on a water bath. The crotonic acid had mostly dissolved after 75mins, at which time 94ml (76g, 0.93 mol) cyclohexene began to be added. It was found that slowly dripping the alkene in to the flask resulted in it merely floating on the surface as the high viscosity of the dense acid mixture prevented the stirrer running at a sufficiently high speed to give efficient incorporation. This problem was overcome by adding the cyclohexene in four portions; each portion was rapidly squirted into the centre of the vortex created by the stirrer resulting in the viscous acid mass being broken down into layers separated by films of cyclohexene. The low viscosity of cyclohexene enabled the layers to slide over each other easily resulting in a great acceleration of

* This early result was calculated with the assumption that the product was near enough 100% HK1. Later experience showed that this assumption was probably erronrous, the HK1 likely to be contaminated by significant quantities of cyclohexyl crotonate, up to 20%. See section 3.3.2.3 for more details.

the mechanical stirrer and very efficient mixing. The cyclohexene addition took ~2 mins. About 1 min later, the reaction began in earnest with mild heat evolution, foaming and rapid refluxing of the cyclohexene (bp 83°C). The reaction was completed rapidly. An extra 10ml cyclohexene was added and stirring at 60°C was continued for another 2 hours.

Total quantity of cyclohexene used = 1.0mol, 104ml, 84g

Workup

500g PPA' contains 415g P_2O_5 = 2.92 mols. To form NaH_2PO_4, 5.85 mols = 234g NaOH is required.

The flask was cooled in ice and 200ml water added. The water layer was agitated until it had become incorporated. 234g NaOH in 300ml water was added in numerous very small portions, with small quantities of liquid nitrogen being added in between to cool the mixture.*† The temperature never rose above 50°C and great care was taken to avoid high local temperatures. (Excessive temperatures during PPA neutralisation were blamed for the extremely low yield obtained during the first HK1 synthesis which was attempted.) The neutralisation took about 90 mins.

Following neutralisation, it was found that the mixture was still too viscous for satisfactory extraction, so 350ml water was added. The mixture was extracted with 200ml PE, then extracted twice with 150ml PE. The extract was washed twice with nearly saturated NaCl solution (200ml, 100ml).

The organic extract contained a substantial quantity of immiscible liquid tar.‡ Some of this could be decanted, and the rest was precipitated as a mysterious light brown spongy semisolid

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* TAKE CARE. Add liquid N_2 only in small lots. Do not stir it too vigorously as otherwise it will dragged under the surface of the acid and cause the latter to splatter. Do not obstruct the flow of nitrogen from the flask. Do not add sodium hydroxide solution if the flow of nitrogen out of the flask is too great as otherwise the NaOH may be sprayed back.

† Conduction of heat to the external ice-bath is so slow with a large-scale work-up like this that as to be wholly inadequate to remove the very considerable heat of neutralisation. Internal cooling is also required. Ice is not satisfactory as the very large quantities required would give an excessive volume of mixture. (Up to ~400g could profitably be added, however, instead of the 350ml addition of water that was made as a result of the mixture being too viscous to separate.) Dry ice is no good as Na_2CO_3 formation causes the sodium hydroxide solution to coagulate as it is added resulting in a mess developing. Liquid nitrogen addition, although it seems rather extreme, seems to be the only heat removal method which allows the neutralisation method to proceed in an hour or two rather than taking all day.

‡ Interestingly, the tar was insoluble in petroleum ether, cyclohexane and diethyl ether.

by the addition of 450ml methanol.* The solid was filtered off. The filtrate was shaken with $NaHCO_3$ and celite† and then filtered again. Most of the solvent was removed using a rotary evaporator, the remaining liquid was dried by stirring with anhydrous $MgSO_4$, subjected to rotary evaporation again and the vacuum distilled.

Distillation Data

Pressure: Steady 0.3 mmHg

Fraction	Water Bath Temperature / °C	Vapour Temperature / °C (Varied with distillation rate)	Mass Obtained / g	Purity. Cyclohexyl Crotonate Content / % by mass (Estimated by NMR)
1	80 – 87	55 (first drops of liquid appeared in condenser) – 70	2.49	~ 40
2	87 – 100	70 – 90	70.79	~ 14
3	100	90 – 75	3.64	Very low

(The liquidity of the residue indicated that the use of an oil bath at > 100°C may have resulted in a larger quantity of ester being collected.)

3.5.3 Experiment 3: The purification of HK1 by the use of semicarbazide

3.5.3.1 Formation of HK1semicarbazone

Semicarbazide hydrochloride (25.0g, 0.226mol) and sodium acetate (anhydrous, 25.0g, 0.305mol) were dissolved in 200ml water and 30.0g crude HK1‡ was added. Ethanol (100 – 130ml) was added until the ketone just dissolved on shaking. (If a small quantity of HK1 separates out and floats on the surface then it does not matter as it will dissolve as the semicarbazone forms.) The reaction was then either run quickly at an elevated temperature (**Method 1**), or it was run slowly at room temperature (**Method 2**).

* Later experience showed that an efficient method for the removal of much of the tar was to shake the organic extract with water and leave it in the separating funnel over the weekend. During this time, the dense tar dropped into the water and emulsified. The aqueous layer could then be run off and disposed of. The same effect did not occur if sodium chloride solution (nearly saturated) was used instead of water as it's higher higher density of, the tar would remain as a distinct layer between the aqueous and PE layers

† It was later found that activated charcoal powder was massively better than celite at absorbing residual tar and brown materials.

‡ The HK1 used contained approximately 14% by mass of cyclohexyl crotonate, as determined by NMR.

Method 1

The HK1/semicarbazideHCl/NaOAc/water/ethanol solution was heated on a 50 – 55°C water bath for 3¼ hours, then stood at room temp for 1¾ hours. A mass of crystals formed. The crystals were removed by filtration, washed with water (30ml) and ethanol (20ml). (The filtrate and washings were combined and left in the dark to see if more HK1semicarbazone would form.) The crystals were washed with a further 50ml ethanol (not added to the filtrate) and dried under vacuum. Yield = 27.17g

The filtrate was kept in the dark at room temperature in a loosely-bunged (to prevent evaporation) flask for 10 days. Crystals formed; they were filtered off, washed with water (40ml) and ethanol (20ml) and dried under vacuum. Yield = 5.82g

Overall yield = 32.99g

= 92% based on the ketone content of the crude HK1 used.

Method 2

This method, which was normally used, proceeded as for **method 1** except that instead of applying heat to the reaction mixture, it was simply left in a dark cupboard for one to three days. It was found that there was little to be gained by leaving the mixture for more than three days. It was only worth keeping the filtrate for a second batch of crystals if the reaction had been run for less than about one and a half days. The yields were similar to **method 1**.

3.5.3.2 Hydrolysis of HK1semicarbazone

54.9g HK1semicarbazone was placed in a medium sized spherical flask. Water (100ml), 10% (~2.9M) aqueous HCl (120ml), cyclohexane (150ml) and a very large stirrer were added and a reflux condenser was fitted. The mixture was heated on an 85°C water bath with extremely vigorous stirring for 1½ hrs.* After cooling to room temperature, the mixture was separated and the aqueous layer extracted twice with cyclohexane (50ml each time). The combined organic solutions were washed with saturated NaCl solution (50ml), concentrated Na_2CO_3 solution (50ml), dried with $MgSO_4$ then filtered. To remove the last traces of water the solution was left over kiln-dried 4Å molecular sieves overnight after which the solvent was removed using a rotary evaporator.

* Note: The use of more concentrated acid, higher temperatures or longer heating times is not satisfactory as it results in a discoloured product. Petroleum spirit is not a satisfactory substitute for cyclohexane because the solubility of HK1 in the former is much lower than in the latter.

Yield = 38.2g = 96% based on the quantity of HK1semicarbazone used. GC-FID indicated a very high purity, estimated from the peak areas as 98% or more.

3.5.3.3 Data on HK1semicarbazone:

$C_{11}H_{17}N_3O$ RMM = 207.28

Melting point: Crystals go brown at 190°C. Due to decomposition, the apparent melting point varies with rate of heating. Typical results obtained are m.p = 217 – 220°C, or with slightly slower heating, m.p = 210 – 215°C.

MS (EI) *m/z, rel.intens. /%*: 207, 84% ($C_{11}H_{17}N_3O^+$), 190, 15% ($-NH_3$), 164, 100% (?).

C,H,N analysis /%: C, 63.73; H, 8.27; N, 20.28 (calculated)

3.5.4 Experiment 4: Preparation of 1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene (HCp1)

A Grignard solution was made under nitrogen by slowly adding 65 g (350 mmol) 1-bromo-3,5-dimethylbenzene to a stirred mixture of 10 g (412 mmol) Mg turnings and 400 ml THF. Gentle heat initiated the reaction after which it briskly refluxed as the magnesium dissolved. When heat generation ceased, the refluxing was continued for five minutes by an external application of heat after which the solution was left to stir and gradually cool down over a period of 30 min. The solution was then cooled in ice and 34.2 g (228 mmol) HK1* was slowly added and the mixture allowed to warm to room temperature and stirred for two hours. The solution was shaken with 150 ml water + 50 ml concentrated hydrochloric acid, then extracted with mixed hexanes (3 × 100 ml). The combined extracts were dried over anhydrous magnesium sulphate and freed of solvent using a rotary evaporator, the product at this stage consisting of brown crystals contaminated by a brown liquid. The volume of liquid was reduced by spreading the material in a thin layer inside a round-bottomed flask and subjecting to vacuum (0.05 mmHg) for 2 hrs. Recrystalisation, which was difficult due to the high solubility of the solid, was achieved with small loss by dissolving the product in not more than 50ml hot (up to an estimated 80°C) petroleum spirit (100-120 °C b.p.) then cooling with dry-ice, filtering and washing with cold (-78°C) petroleum spirit (3 lots, 100 ml in total). The product was freed of solvent by atmospheric evaporation followed by drying in vacuo.

* The HK1 used had been distilled but not purified using semicarbazide. It therefore contained cyclohexyl crotonate impurity.

Yield = 19.5 g, 36 %*

3.5.4.1 Data characterising HCp1

Appearance: Large crystals – colourless and transparent; small crystals or powder – white.

m.p.: 90-92°C

Analysis: Calc. For $C_{18}H_{22}$ (238.37): C, 90.70; H, 9.30. Found: C, 90.47; H, 9.34.

MS (EI) *m/z*: 238 (strongest peak, M^+).

IR (Nujol mull) /cm^{-1}: 1597 (m, sh), no notable features.

^{1}H-NMR δ /ppm ($CDCl_3$): 1.19 (dd, 1H, J = 7.4Hz and 15 Hz), 1.57 (s, 2H), 1.67 (s 2H), 1.95 (s, 1H), 2.175 (s, 6H, aryl CH_3), 2.31 (3H, alkenyl CH_3), 2.41 (bs, 1H), 2.71 (bs, 1H), 3.22 (unresolved m, 1H), 6.80 (s, 1H, aryl H), 7.01 (s, 2H, aryl H). 1 H is unaccounted for.

^{13}C{^{1}H} NMR δ /ppm ($CDCl_3$): 13.1, 21.4, 23.2, 24.0, 27.2, 46.0, 124.5, 126.8, 137.5. 6C are unaccounted for.

3.5.5 Experiment 5: Preparation of (R,S)-1-(3,5-dimethylphenyl)-2-(trimethylsilyl)-3-methyl-4,5,6,7-tetrahydro-2H-indene. (TMSCp1)

A solution of 5 g (21.0 mmol) HCp1 in 60 ml THF was prepared under nitrogen and cooled in ice. 12 ml (30 mmol) BuLi solution (2.5M in mixed hexanes) was added and a red colour was quickly produced. The solution was cooled in dry-ice and stirred for a further 3 hrs after which 3.8 g (4.5 ml, 35 mmol) trimethylsilyl chloride was added. The solution was warmed to room temperature and stirred for a further 1 hr. THF and excess Me_3SiCl were removed under vacuum and the product was extracted with dichloromethane (2 × 30 ml). The solvent was removed on a rotary evaporator to leave thick oil. To allow this to crystallise and to assist purification, it was found necessary to leave it under vacuum (0.05 mmHg) for at least 6 hrs to remove some of the oily impurity. The resulting brownish crystalline mass was found to possess extreme solubility in non-polar solvents and to readily form supercooled solutions making recrystalisation without great loss highly difficult. The following method was satisfactory: The crystalline mass was dissolved in the minimum volume of hot (up to ~70°C) petroleum spirit (100-120°C b.p.). (Trial and error was used to determine the correct quantity,

* The yield was calculated on the assumption that the HK1 used was pure whereas it in fact contained cyclohexyl crotonate impurity in an unknown proportion, possibly as much as 20% by mass. The use of semicarbazide-purified HK1 would no doubt have given much better results, not least by much reducing the quantity of impurities which needed to be separated from the product. (The high solubility of HCp1 meant that the losses in trying to crystalise it from a large quantity of impurities were no doubt high.) Wastage of Grignard reagent would also be reduced, particularly since esters react with Grignards in a 1:2 molar ratio.

roughly estimated as about 2-4 ml.) The most reliable way to induce crystalisation was to freeze the mixture to an amorphous mass using dry-ice then thaw at room temperature. When crystalisation at room temperature was complete, further crystalisation was achieved by recooling in dry-ice and stirring. The paste was filtered and washed with cold (-78°C) petroleum spirit (about 3 ml) to leave fine off-white crystals. When required, the purity of the crystals could be further slightly increased by crushing between filter papers to absorb the adhering liquid. Residual solvent was removed under vacuum.
Yield = 4.2g, 64% of off-white crystals of m.p 77-78°C.

An alternative recrystallisation procedure involved dissolving the crude product in hot mixed hexanes, cooling in the freezer and then in dry-ice, removing the liquid using a filter-cannula and crushing the crystals between filter papers before the solvent evaporatated. The yield was increased to 70%, but the melting point of the (light yellow) crystals was only 66-77°C.

3.5.5.1 Data characterising TMSCp1

Appearance: Very impure – yellow; decent purity – off-white; large crystals – clear and colourless, pure white when crushed.
m.p.: 77-78 °C
MS (EI) *m/z, rel.intens. /%*: 310, 100% (M^+); 295, 6% (M^+ - CH_3); 236, 55% (M^+ - $HSiMe_3$); 73, 67% ($^+SiMe_3$).
1H-NMR δ /ppm ($CDCl_3$): 1.19 (dd, 1H, J = 7.4 Hz and 15 Hz), 1.57 (s, 2H), 1.67 (s, 2H), 1.95 (s, 1H), 2.175 (s, 6H, aryl CH_3), 2.31 (3H, alkenyl CH_3), 2.41 (bs, 1H), 2.71 (bs, 1H), 3.22 (unresolved m, 1H), 6.80 (s, 1H, aryl H), 7.01 (s, 2H, aryl H). 1 H is unaccounted for.

3.5.6 Experiment 6: Preparation of substituted ferrocenes {*bis*-η⁵-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II) ((Cp1)₂Fe) and η⁵-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]-η⁵-[1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]iron(II) (Cp1Cp2Fe)} and their separation

A solution containing 0.5 g HCp1 in 30 ml diethyl ether was prepared under nitrogen. BuLi (0.84 ml, 0.21 mmol (2.5M in mixed hexanes)) was added and the mixture stirred for 2 ½ hrs. A suspension of 0.19 g anhydrous $FeCl_2$ in 30 ml THF was prepared and added to the lithiated ligand solution *via* a cannula. The resulting clear orange solution was stirred overnight. The

solvent was removed under vacuum and the solid extracted with mixed hexanes (2×30ml). The resulting solution was evaporated under vacuum to give an orange solid. Yield = 0.10g.

A chromatography column of 3.5 cm internal diameter was filled with silica (Merck Kieselgel 60. Powdered silica gel, particle size 0.040-0.063 mm) to a depth of 18 cm and then evacuated for 15 mins and backfilled with nitrogen. The purging process was repeated several times, after which the column was saturated with nitrogen-sparged mixed-hexanes. The orange solid was dissolved in the minimum volume of mixed-hexanes, added to the column and eluted with air-free mixed hexanes. The material separated into a mobile orange band and a thin red band which remained immobile at the top of the column. The orange band was collected, after which the red material was extracted with an air-free mixture of 30 vols Et_2O and 170 vols mixed hexanes. Some of the product decomposed on the column to give a powerfully adsorbed green substance, probably containing ferrocenium ions. The green substance could be partially removed using EtOH. The orange and red solutions, which were not air sensitive, had the solvent removed from them using a rotary evaporator and were subsequently dried under vacuum (0.05mmHg). Yields: Orange ferrocene ($(Cp1)_2Fe$), 0.06 g, 7.5 %; red ferrocene (Cp1Cp2Fe), <0.02 g.

3.5.6.1 Data characterising orange ferrocene $(Cp1)_2Fe$

Appearance: Orange powder or crystals. A large crystal was grown, but due to the relatively uninteresing nature of the compound a crystal structure determination was not attempted.

Analysis: Calc. For $C_{36}H_{42}Fe$ (530.58): C, 81.49; H, 7.98. Found: C, 80.60; H, 8.46.

MS (EI) *m/z, rel.intens. /%*: 530, 100% (M^+); 129, 44%; 57, 52%.

^{1}H-NMR δ /ppm ($CDCl_3$): 1.18 (s, 1H), 1.3-1.7 (m), 1.9-2.3 (m), 3.72 (s, 1H, cyclopentadienyl H), 6.7 (m, 3H, aryl H).

3.5.6.2 Data characterising red ferrocene Cp1Cp2Fe.

Appearance: small blood-red crystals.

MS (EI) *m/z*: 558 (M^+).

High resolution MS (EI) : molc mass = 558.266244 Da.

Possible Assignments.	Calculated Mass /Da	Error in ppm*
$C_{33}H_{50}Fe_2$	558.261131	-9.2
$C_{38}H_{46}Fe$	558.294891	51.3
$C_{36}H_{42}FeN_2$	558.269739	6.3
$C_{36}H_{42}FeNO$	558.245929	-36
$C_{37}H_{42}FeO$	558.258505	-13.9

*Error in ppm = [{(calc. mass)-(actual mass)}/(actual mass)] $\times 10^6$. The correct formula should give an error of less than approximately 3ppm.

The last formula in the table turned out to be correct by X-ray structure determination.

^{1}H-NMR δ /ppm ($CDCl_3$): 0.6-2.2 (series of m); 6.6-7 (aryl H).

3.5.7 Experiment 7: Preparation of η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indenyl]trichlorotitanium(IV) (Cp1$TiCl_3$)

The preparation was carried out under nitrogen.

TMSCp1 (1 g, 3.2 mmol) was dissolved in 20 ml mixed hexanes and titanium tetrachloride solution (5 ml, 1M, toluene) was added with stirring. A brown suspension immediately resulted. Stirring was continued for 10 mins, after which vacuum was applied to remove solvent, Me_3SiCl and excess $TiCl_4$. The solid residue was extracted with two lots of dichloromethane (40 ml and 40 ml), giving dark red solutions. The solvent was removed from the separate extracts under vacuum, giving dark red/black solids. The second extract gave little solid and was disposed of. The residue from the extractions was also subjected to vacuum. Yield of insoluble residue = 0.08g; yield of red/black solid (Cp1$TiCl_3$)from first extraction = 1.30g.

The Cp1$TiCl_3$ was recrystallised by dissolving in a very small volume of dichloromethane and floating mixed hexanes on top. Unfortunately, the crystals produced were of flaky habit and not suitable for structure determination.

3.5.7.1 Data characterising $Cp1TiCl_3$

Appearance: Dark red/black flaky crystals

MS (EI) *m/z, rel.intens. /%*: 474, 5% ($C_{36}H_{42}$, dimerised ligand); 392, 8% (M+); 358, 25% (absent in some samples); 240, 100% (isotope ratio indicates Ti present, however, this peak is absent in another spectrum, a peak at 237 replacing it. 237 = $C_{18}H_{21}^+$? – seems unlikely since it would be antiaromatic.); 225, 50%; 211, 45%; 197, 35%; 119, 35%; 91, 90% (tropyllium cation).

^{1}H-NMR δ /ppm (CD_2Cl_3): 1.6-2.2 (m, 6H (probably includes impurity peaks), 2.39 (s, 6H, aryl CH_3), 2.45 (s, 3H, cyclopentadienyl CH_3); 2.62-2.8 (dt, 1H), 2.86-3.04 (dt, 1H), 3.16-3.34 (dt, 1H), 3.58-3.76 (m, 1H) (there are sharply resolved couplings in these four multiplets, but they have not yet been assigned); 7.06 (s, 1H, aryl H or Cp H? (rather too high to be the latter), 7.28 (s, 1H, aryl H), 7.33 (s, 2H, aryl H).

^{13}C{^{1}H} NMR δ /ppm (CD_2Cl_2): 16.0, 21.3, 21.4, 26.0, 28.0, 121.4, 125.9, 131.1, 133.8, 137.2, 138.5, 139.8, 141.3, 142.0. (All 15 carbons shown.)

3.6 References for chapter 3

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4 Appendices

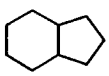
4.1 Appendix 1: Naming of substituted hydroindenes

4.1.1 Introduction

This appendix gives a few useful basic principles for the naming of hydroindenes. The hydroindene skeleton is the basis of many of the compounds synthesised for the experimental part of this thesis.

The nomenclature in this appendix has been derived from the rules and guidelines set out in the very excellent book by Fox and Powell.[1] This should be consulted for rules as to how to assign locants etc

Figure 1. The basic skeleton of a substituted hydroindene



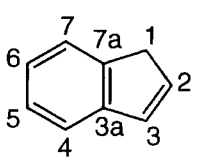
There are two correct systems for the naming of substituted hydroindenes. They can either be named using arene nomenclature, i.e. as indenes, or they can be named as bicyclo[4.3.0]nonanes using alicyclic nomenclature. The arene nomenclature is a clear favourite amongst organometallic chemists as it is easily extended to naming ligands within a complex by replacing *–indene* with *–indenyl* and using the η^5 prefix.

4.1.2 Arene nomenclature

In this system of nomenclature, aromatic compounds and hydrogenated arenes are named as additive/substitutive derivatives of the largest or most highly substituted and central standard named aromatic unit. For the substituted hydroindenes which this project is concerned with, the base compound is a double bond isomer of indene, the particular isomer being shown by the use of a numbered, italicised *indicated hydrogen* in the name.

Note: An indicated hydrogen is not a substituent. The presence of the hydrogen is implicit in the name indene, it is only the position which needs to be specified unambiguously.

Figure 2. 1*H*-Indene, showing the standard numbering system



The 1*H* in the name 1*H*-indene shows that the indicated hydrogen is at position 1, or to put it another way, that the only non-doubly bonded carbon atom is at position 1. The use of the

indicated hydrogen descriptor will be demonstrated by a couple of further examples, Figure 3 and Figure 4.

Figure 3. 2*H*-Indene

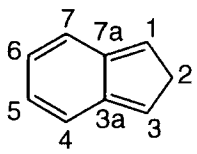
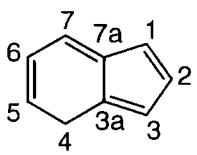


Figure 4. 4*H*-Indene



Substituted hydroindenes are named as derivatives of the relevant indene isomer using the usual additive/substitutive rules. Figure 5 shows an example.

Figure 5. 6,7-Dihydro-3a-methyl-3a*H*-indene

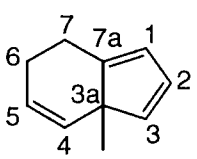
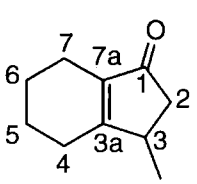


Figure 6 shows the naming and numbering of a ketone which was much used in the experimental work.

Figure 6. 3-methyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-one



(For the application of alicyclic nomenclature to the above compound, see Figure 10.)

The above compound could conceivably be named as a tetrahydroindan. Indan (also called indane) (Figure 7) is 2,3-dihydro-1*H*-indene. However, indan, unlike indene, is classified as a trivial name and is thus not suitable for use as the basis for a systematic name.

Figure 7. Indan or Indane

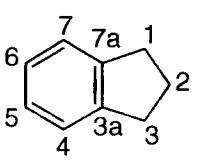
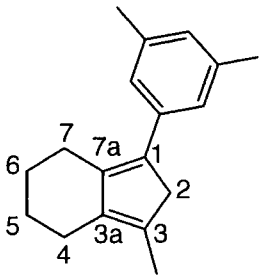


Figure 8. 1-(3,5-dimethylphen-1-yl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene, or 1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2*H*-indene



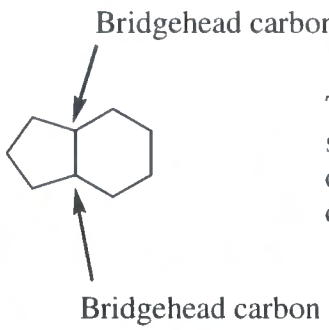
(For the application of alicyclic nomenclature to the above compound, see Figure 11.)

The aryl substituent can be named *3,5-dimethylphen-1-yl*, but this is rather pedantic and makes the name sound less sonorous than when the alternative *3,5-dimethylphenyl* is used. The simplification can be made without introducing any ambiguity as in the nomenclature of substituents bearing their own numbered sub-substituents, the number of the atom in the substituent which is joined to the main body of the compound is always assigned as 1 unless specifically indicated otherwise.

4.1.3 Alicyclic nomenclature

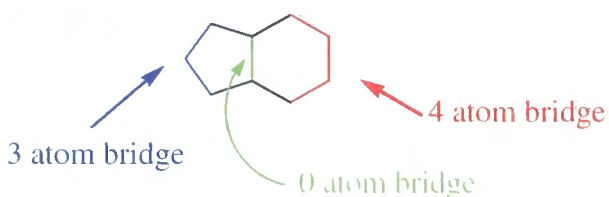
The basic hydroindene framework is named bicyclo[4.3.0]nonane using alicyclic nomenclature. The basic principles behind the derivation of this name are illustrated in Figure 9.

Figure 9. Alicyclic nomenclature as applied to perhydroindene

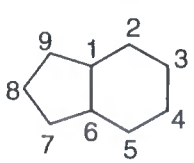


The first stage in naming a polycyclic system is to identify the bridgehead carbons. This is easy in the present case as there are only two

The structure is drawn with the largest bridge on the right, the second largest on the left and the smallest in the middle.



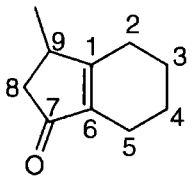
Numbering is now applied anticlockwise starting from the top bridgehead position, thus:



The name of the compound is derived as follows:
1] At least two bond severances required to produce acyclic system => *bicyclo*
2] Nine carbon atoms within ring system => *nonane*
3] One 4-atom bridge, one 3-atom bridge and one 0-atom bridge => *[4.3.0]*
4] Combine to produce name *bicyclo[4.3.0]nonane*

The next few figures show how alicyclic nomenclature is applied to some of the compounds discussed in the experimental section of this thesis.

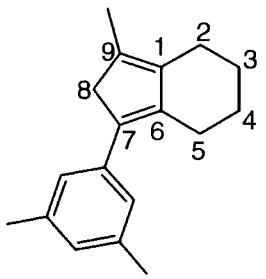
Figure 10. 9-Methylbicyclo[4.3.0]non-1(6)-en-7-one



(For the application of arene nomenclature to the above compound, see Figure 6.)

The naming of 9-methylbicyclo[4.3.0]non-1(6)-en-7-one (Figure 10) requires a small amount of explanation. The locant for the double bond is 1(6) to indicate that the bond runs from carbon 1 to 6; using the locant "1" would be erroneous in this situation as it defines a double bond running between carbons 1 and 2. It will also be noticed that the lower locant, 7, is applied to the ketone group rather than the methyl as the former has the higher priority.

Figure 11. 7-(3,5-dimethylphenyl)-9-methylbicyclo[4.3.0]nona-6,9(1)-diene



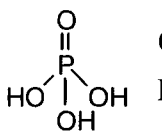
(For the application of alicyclic nomenclature to the above compound, see Figure 8.)

4.2 Appendix 2: Notes on the composition and synthesis of polyphosphoric acid (PPA)

4.2.1 Introduction

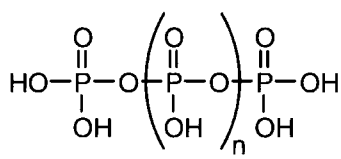
Polyphosphoric acid is an extremely viscous syrup with a composition in-between liquid orthophosphoric acid and the glassy solid metaphosphoric acid.

Figure 12. Phosphoric(V) acids



Orthophosphoric acid H_3PO_4

Polyphosphoric acids



n	Name of Acid
0	Diphosphoric
1	Triphosphoric
2	Tetraphosphoric
Large	Metaphosphoric

For metaphosphoric acid, n is so large, maybe 1000 or more, that HPO_3 is used as a essentially entirely accurate empirical formula.

Polyphosphoric acid can be made by the simple process of dissolving phosphorus pentoxide in hot orthophosphoric acid until the desired composition is reached, or it can be purchased. Standard concentration polyphosphoric acid has a phosphorus content equal to 115% of that of H_3PO_4, or to put it another way, the hydrolysis of 100g polyphosphoric acid will give 115g orthophosphoric acid. As will shortly be shown, this concentration is equivalent to 83% P_2O_5 by mass. Standard concentration polyphosphoric acid will henceforth be referred to as PPA'.

Due to a delay in the supply of PPA', the author calculated the composition of PPA' in terms of P_2O_5 and H_2O and determined the proportions necessary to produce PPA' from standard concentration H_3PO_4* and phosphorus pentoxide. A calculation was also done for interest to see what the degree of polymerisation might be expected in the species present in PPA'. The calculations are relatively simple, but because the results may be of some use, they will now be given:

4.2.2 The composition of PPA'

Standard concentration polyphosphoric acid, PPA', is equivalent to 115% H_3PO_4.

Species	RMM
H_3PO_4	98.0
P_2O_5	141.95
H_2O	18.02

$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$

Species	RMM
P_2O_5	141.95
$3(H_2O)$	54.06
$2(H_3PO_4)$	196

Now, 100g PPA' + 15g $H_2O \rightarrow$ 115g H_3PO_4
Using the above relative molecular masses, it can be shown that 115g H_3PO_4 contains 31.72g H_2O and 83.29g P_2O_5.

Now, we know that 100g PPA' + 15g $H_2O \rightarrow$ 115g H_3PO_4
Therefore, <u>100g PPA'</u> = 115g H_3PO_4 – 15g H_2O
= 83.29g P_2O_5 + (31.72 – 15)g H_2O
= <u>83.29g P_2O_5 + 16.72g H_2O.</u>

The most practical method of producing PPA' in the lab is to add P_2O_5 to H_3PO_4, rather than removing water from the latter. (The dehydration of H_3PO_4 requires high temperatures and the hot acid is very corrosive to metals and somewhat corrosive to glass.)

100g PPA' contains 16.72g H_2O
If forming from P_2O_5 and H_3PO_4 then all the water has to come from the latter.
16.72g water is contained in (16.72÷31.72)×115 = 60.62g H_3PO_4
60.62g H_3PO_4 contains (16.72÷31.72)×83.29 = 43.90g P_2O_5
So to make <u>100g PPA'</u>, <u>60.62g H_3PO_4</u> and (83.29 – 43.90) = <u>39.39g P_2O_5</u> are required.

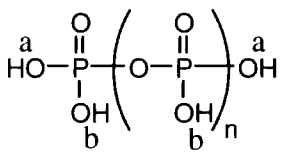
* The standard syrupy phosphoric acid found in labs contains 85% orthophosphoric acid by weight.

Standard lab H_3PO_4 contains 85% orthophosphoric acid by weight. Call this SPA (Syrupy Phosphoric Acid, a term used in some old chemistry books.)
100g SPA contains 15g H_2O and 85g H_3PO_4
85g H_3PO_4 contains (85÷115)×31.72 = 23.44g H_2O and (85÷115)×83.29 = 61.56g P_2O_5
Therefore, 100g SPA contains 61.56g P_2O_5 and (15 + 23.44) = 38.44g H_2O
100g PPA' contains 16.72g H_2O and 83.29g P_2O_5. If forming from P_2O_5 and H_3PO_4 then all the water has to come from the latter.
(16.72÷38.44)×100 = 43.50g SPA
43.50g SPA contains (16.72÷38.44)×61.56 = 26.78g P_2O_5
So to make 100g PPA', 43.50g SPA and (83.29 – 26.78) = 56.51g P_2O_5 are required.

4.2.3 Degree of polymerisation of PPA'

It is interesting and easy to do a calculation to determine the chain lengths we might expect to be prominent amongst the polyphosphoric acids in PPA'. The following calculation assumes that the average chain length is determined, to a first approximation, by simple statistics with energetic factors not making any particular chain lengths particularly favoured relative to others.

Figure 13. Diagram to go with calculations on the degree of polymerisation of PPA'



n = number of repeating —O—P(O)(OH)— units
n = 0 => orthophosphoric acid, n = 1 => diphosphoric acid, etc.
a and b label the adjacent hydroxyl groups

mols $P(OH)_2(O)[OP(OH)(O)]_nOH$ = m
mols OHa = 2m
mols OHb = m(n + 1)
So (mols OHb) ÷ (mols OHa) = (n + 1) ÷ 2
So n = 2[(mols OHb) ÷ (mols OHa)] – 1

100g PPA' contains 83.29g P_2O_5 and 16.72g H_2O.
= 0.5868 mol P_2O_5 + 0.9279 mol H_2O
Therefore we have 1.174 mol P => 1.174 mol OHb
0.9279 x 2 = 1.856 mol OH (a and b)
1.856 – 1.174 = 0.682 mol OHa
Using the formula derived above, n = [2×(1.174 ÷ 0.682)] – 1
= 2.44

The result n = 2.44 indicates that the most predominant species present in PPA' would probably be triphosphoric and tetraphosphoric acids in roughly equal proportions.

4.2.4 Preparation of PPA' in the lab

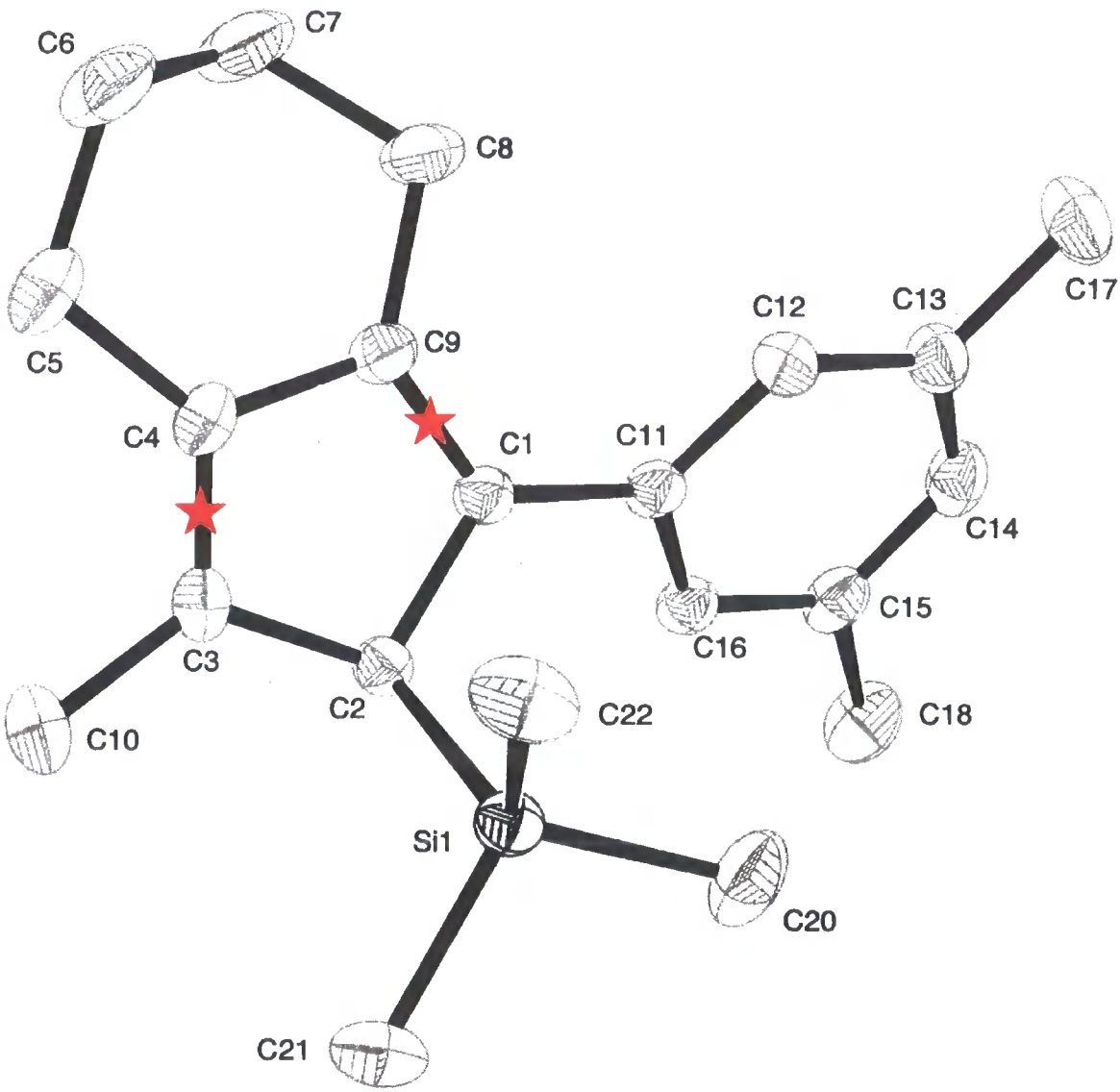
Standard syrupy phosphoric acid (85% H_3PO_4 by wt.) (87 g) was placed in a large round-bottomed flask fitted with a slow mechanical stirrer. Phosphorus pentoxide (113 g) was added in small lots, care being taken with the first lots due to the heat evolved. When a large proportion of the phosphorus pentoxide had been added, the mixture became very viscous and dissolution of the solid was very slow but heating to 150°C solved the problem. The mixture was used for Nazarov reactions when it became homogenous. Total preparation time ~2h.

4.3 Appendix 3: The structure of TMSCp1, (R,S)-1-(3,5-dimethylphenyl)-2-(trimethylsilyl)-3-methyl-4,5,6,7-tetrahydro-2H-indene, as determined by X-ray crystallography.

CIF: 00SRV137*

Space Group: P-1

Figure 14. The molecular structure of TMSCp1



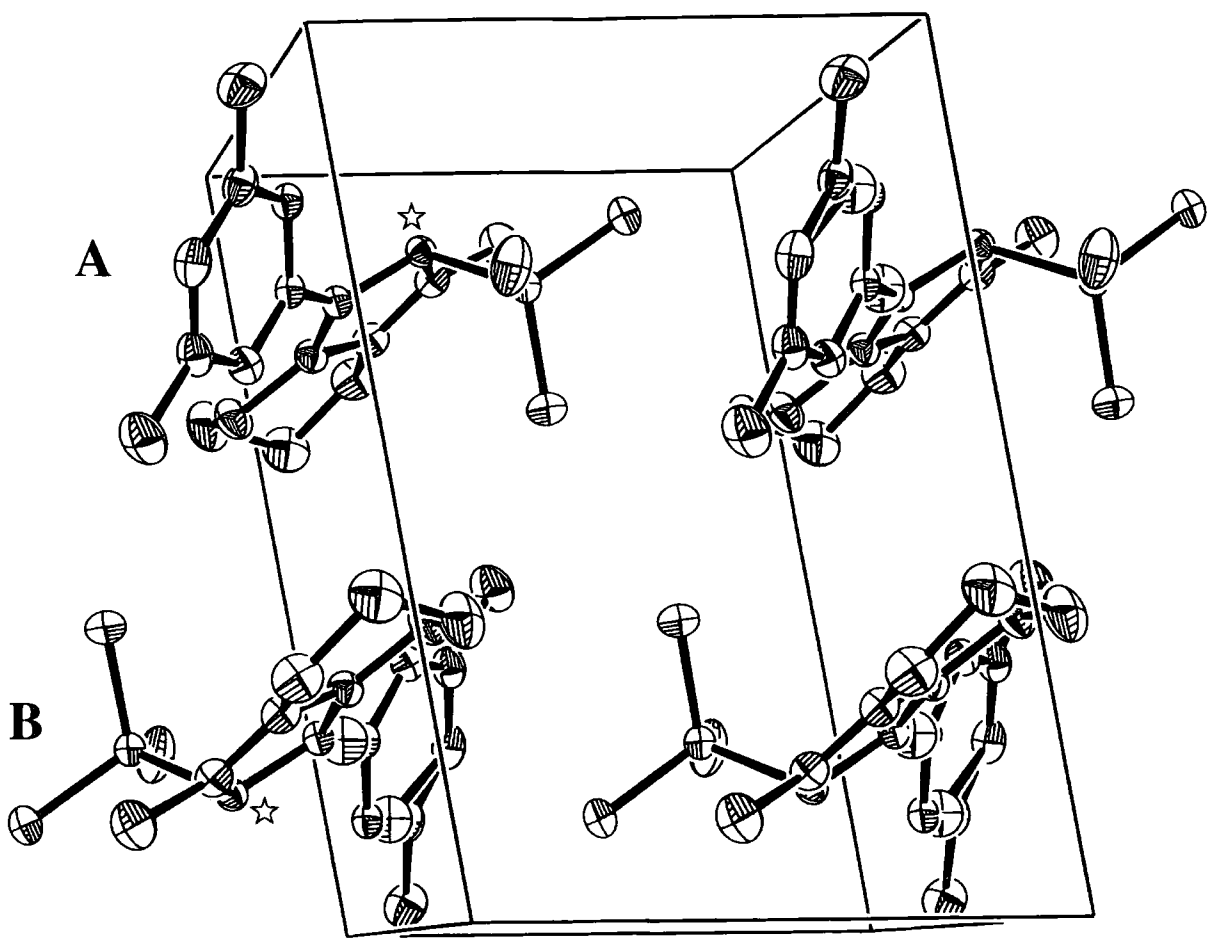
★ = Double bond

* H. Puschmann, Durham University Crystallography Department, 16.02.2000

Bond Lengths

Bond	Length /Å
C1 – C2	1.5038(12)
C2 – C3	1.4984(13)
C3 – C4	1.3546(14)
C4 – C9	1.4580(13)
C9 – C1	1.3682(12)

Figure 15. A view of the unit cell of TMSCp1 showing the two enantiomers



This view of the unit cell is perpendicular to the (0,1,0) plane.

☆ = Chiral carbon atom.

A and **B** are the two enantionmers.

Figure 16. A view of the unit cell of TMSCp1, looking perpendicular to the (001) plane.

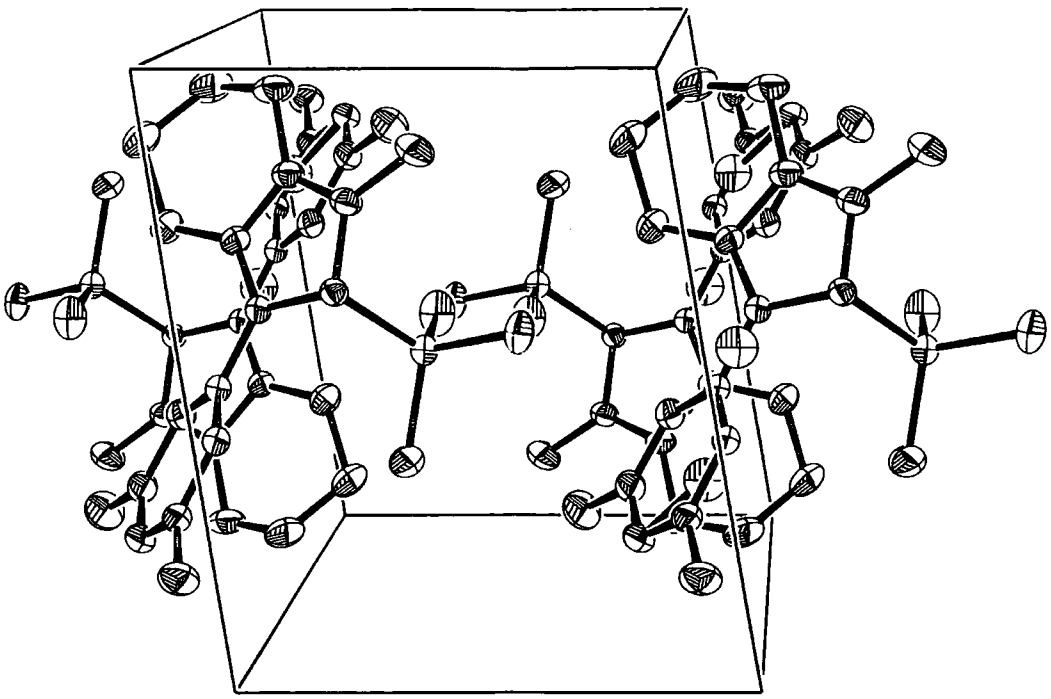
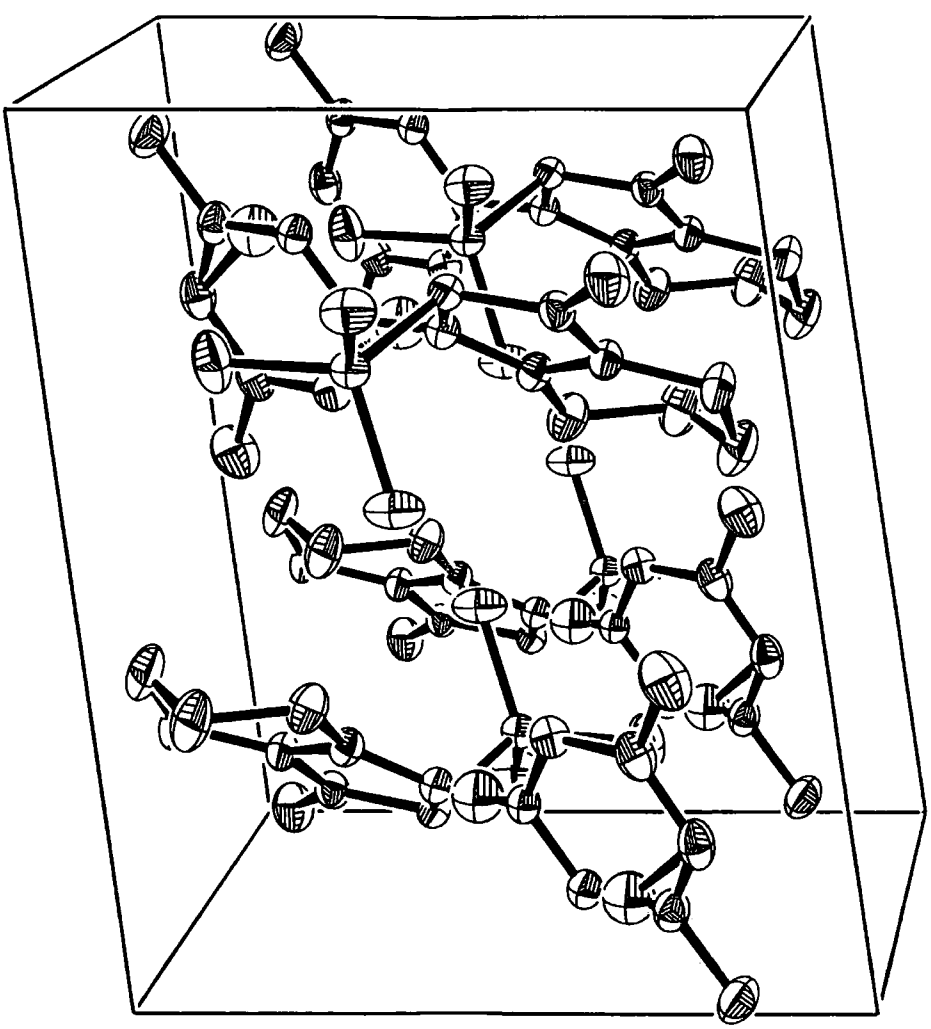


Figure 17. A view of the unit cell of TMSCp1, looking perpendicular to the (100) plane.



4.3.1 Complete crystallographic information for TMSCp1 (also refer to the diagrams reproduced above (figs. 14 - 17))

cif file for 00srv137

Horst.Puschmann@Durham.ac.uk - 16/02/2000

Table 1. Crystal data and structure refinement for 00srv137.

Identification code	00srv137	
Empirical formula	C21 H30 Si	
Formula weight	310.54	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.2719(4) Å	α= 98.2270(10)°.
	b = 9.9228(5) Å	β= 99.7160(10)°.
	c = 12.2382(6) Å	γ = 99.6260(10)°.
Volume	960.88(8) $Å^3$	
Z	2	
Density (calculated)	1.073 Mg/m^3	
Absorption coefficient	0.119 mm^{-1}	
F(000)	340	
Crystal size	0.7 x 0.5 x 0.3 mm^3	
Theta range for data collection	1.72 to 30.45°.	
Index ranges	-11<=h<=11, -13<=k<=14, -17<=l<=17	
Reflections collected	11456	
Independent reflections	5236 [R(int) = 0.0268]	
Completeness to theta = 30.45°	89.8 %	
Absorption correction	Extinction	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5236 / 0 / 320	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.1032	
R indices (all data)	R1 = 0.0405, wR2 = 0.1070	
Extinction coefficient	0.000(2)	
Largest diff. peak and hole	0.362 and -0.197 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 00srv137. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(7)	-1149(2)	8373(2)	6530(1)	49(1)
C(20)	3480(2)	3105(1)	7742(1)	46(1)
C(6)	406(2)	9276(2)	6319(1)	49(1)
C(17)	-3536(2)	1683(2)	5605(1)	47(1)
C(22)	4287(2)	5316(2)	6324(1)	42(1)
C(5)	1931(2)	9329(1)	7233(1)	40(1)
C(18)	-828(2)	1723(1)	9631(1)	41(1)
C(10)	4913(2)	8518(1)	8819(1)	40(1)
C(21)	6341(1)	5494(1)	8694(1)	36(1)
C(8)	-953(1)	6853(1)	6437(1)	36(1)
C(13)	-2284(1)	2388(1)	6662(1)	32(1)
C(12)	-1220(1)	3645(1)	6686(1)	28(1)
C(14)	-2161(1)	1785(1)	7626(1)	33(1)
C(9)	632(1)	6746(1)	7195(1)	26(1)
C(1)	1016(1)	5671(1)	7709(1)	22(1)
C(15)	-1008(1)	2410(1)	8605(1)	29(1)
C(3)	3278(1)	7580(1)	8252(1)	26(1)
C(4)	2029(1)	7925(1)	7545(1)	27(1)
C(11)	-72(1)	4323(1)	7666(1)	23(1)
C(2)	2775(1)	6097(1)	8380(1)	22(1)
C(16)	16(1)	3685(1)	8619(1)	25(1)
Si(1)	4214(1)	4995(1)	7775(1)	24(1)

Table 3. Bond lengths [Å] and angles [°] for 00srv137.

C(7)-C(6)	1.523(2)
C(7)-C(8)	1.5344(17)
C(20)-Si(1)	1.8649(13)
C(6)-C(5)	1.526(2)
C(17)-C(13)	1.5098(16)
C(22)-Si(1)	1.8577(12)
C(5)-C(4)	1.5076(14)
C(18)-C(15)	1.5104(15)
C(10)-C(3)	1.5015(14)
C(21)-Si(1)	1.8673(11)
C(8)-C(9)	1.5012(14)
C(13)-C(14)	1.3935(16)
C(13)-C(12)	1.3942(14)
C(12)-C(11)	1.4021(13)
C(14)-C(15)	1.3904(16)
C(9)-C(1)	1.3682(12)
C(9)-C(4)	1.4580(13)
C(1)-C(11)	1.4709(12)
C(1)-C(2)	1.5038(12)
C(15)-C(16)	1.3957(13)
C(3)-C(4)	1.3546(14)
C(3)-C(2)	1.4984(13)
C(11)-C(16)	1.4017(13)
C(2)-Si(1)	1.9131(9)
C(6)-C(7)-C(8)	110.63(11)
C(7)-C(6)-C(5)	111.52(11)
C(4)-C(5)-C(6)	112.30(10)
C(9)-C(8)-C(7)	110.30(10)
C(14)-C(13)-C(12)	118.88(9)
C(14)-C(13)-C(17)	120.49(11)
C(12)-C(13)-C(17)	120.63(11)
C(13)-C(12)-C(11)	121.24(9)
C(15)-C(14)-C(13)	121.50(9)
C(1)-C(9)-C(4)	109.10(8)
C(1)-C(9)-C(8)	129.80(9)

C(4)-C(9)-C(8)	121.01(9)
C(9)-C(1)-C(11)	127.63(8)
C(9)-C(1)-C(2)	108.54(8)
C(11)-C(1)-C(2)	123.81(8)
C(14)-C(15)-C(16)	118.68(9)
C(14)-C(15)-C(18)	121.29(10)
C(16)-C(15)-C(18)	120.02(10)
C(4)-C(3)-C(2)	109.09(8)
C(4)-C(3)-C(10)	126.02(10)
C(2)-C(3)-C(10)	124.90(9)
C(3)-C(4)-C(9)	109.53(8)
C(3)-C(4)-C(5)	127.74(10)
C(9)-C(4)-C(5)	122.42(10)
C(16)-C(11)-C(12)	118.22(9)
C(16)-C(11)-C(1)	120.24(8)
C(12)-C(11)-C(1)	121.54(8)
C(3)-C(2)-C(1)	103.57(7)
C(3)-C(2)-Si(1)	110.39(6)
C(1)-C(2)-Si(1)	111.05(6)
C(15)-C(16)-C(11)	121.45(9)
C(22)-Si(1)-C(20)	109.68(7)
C(22)-Si(1)-C(21)	110.96(6)
C(20)-Si(1)-C(21)	106.83(7)
C(22)-Si(1)-C(2)	108.14(5)
C(20)-Si(1)-C(2)	112.21(5)
C(21)-Si(1)-C(2)	109.04(5)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 00srv137. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(7)	45(1)	44(1)	68(1)	26(1)	7(1)	23(1)
C(20)	41(1)	27(1)	75(1)	7(1)	25(1)	12(1)
C(6)	58(1)	39(1)	58(1)	28(1)	11(1)	19(1)
C(17)	38(1)	39(1)	50(1)	-8(1)	-6(1)	-3(1)
C(22)	38(1)	63(1)	25(1)	7(1)	7(1)	12(1)
C(5)	52(1)	24(1)	47(1)	15(1)	13(1)	9(1)
C(18)	49(1)	35(1)	48(1)	20(1)	19(1)	8(1)
C(10)	36(1)	28(1)	47(1)	0(1)	2(1)	-5(1)
C(21)	25(1)	53(1)	33(1)	9(1)	3(1)	14(1)
C(8)	31(1)	37(1)	42(1)	16(1)	0(1)	12(1)
C(13)	25(1)	26(1)	39(1)	-2(1)	3(1)	3(1)
C(12)	25(1)	27(1)	30(1)	4(1)	3(1)	5(1)
C(14)	28(1)	22(1)	48(1)	4(1)	12(1)	2(1)
C(9)	25(1)	25(1)	28(1)	8(1)	5(1)	7(1)
C(1)	20(1)	22(1)	25(1)	5(1)	4(1)	4(1)
C(15)	27(1)	25(1)	39(1)	10(1)	13(1)	8(1)
C(3)	28(1)	21(1)	29(1)	2(1)	7(1)	1(1)
C(4)	33(1)	21(1)	30(1)	8(1)	9(1)	6(1)
C(11)	19(1)	22(1)	28(1)	5(1)	6(1)	5(1)
C(2)	21(1)	22(1)	23(1)	5(1)	3(1)	3(1)
C(16)	22(1)	24(1)	29(1)	7(1)	6(1)	6(1)
Si(1)	21(1)	27(1)	24(1)	4(1)	5(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 00srv137.

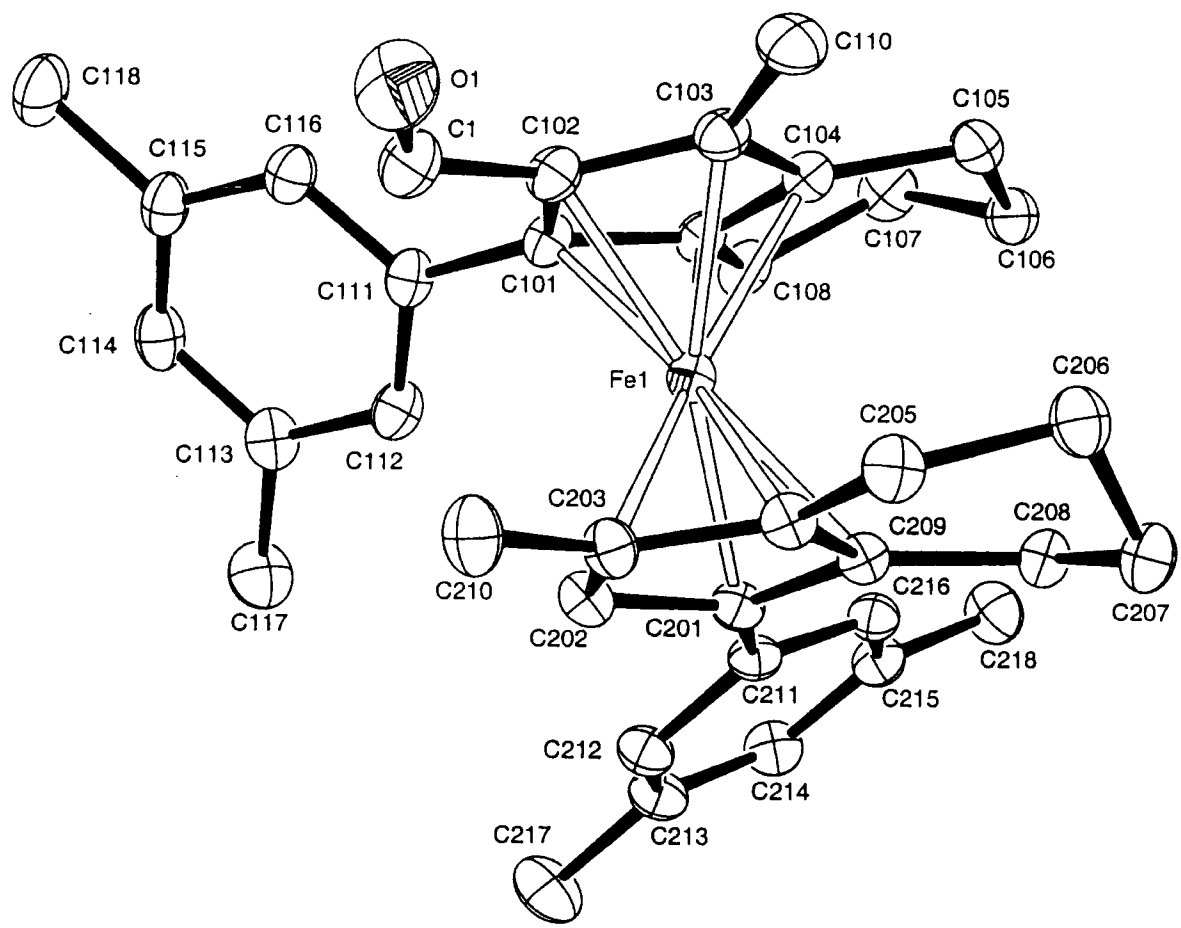
	x	y	z	U(eq)
H(5A)	2940(20)	9723(17)	6986(13)	49(4)
H(10B)	5820(20)	8400(19)	8406(15)	60(5)
H(6A)	630(20)	8883(17)	5580(14)	52(4)
H(8B)	-1943(19)	6273(16)	6585(13)	43(4)
H(10C)	4810(20)	9500(20)	8906(15)	61(5)
H(14)	-2890(20)	903(16)	7597(13)	48(4)
H(8A)	-920(20)	6492(16)	5664(14)	46(4)
H(16)	803(16)	4124(14)	9298(11)	30(3)
H(2)	2895(17)	6022(14)	9197(11)	32(3)
H(12)	-1217(17)	4048(15)	6027(12)	34(3)
H(21C)	6980(20)	6380(20)	8588(16)	69(5)
H(7A)	-2100(20)	8409(18)	6007(15)	60(5)
H(6B)	220(20)	10250(18)	6298(14)	56(5)
H(20C)	2430(20)	2740(20)	7195(16)	64(5)
H(7B)	-1320(20)	8712(18)	7317(15)	54(5)
H(10A)	5290(20)	8328(19)	9586(16)	60(5)
H(21A)	6280(20)	5640(20)	9496(17)	71(6)
H(5B)	1850(20)	9977(18)	7913(14)	52(4)
H(22A)	4920(30)	4710(20)	5955(18)	79(6)
H(20A)	4290(20)	2640(20)	7536(16)	68(5)
H(21B)	7010(20)	4770(20)	8532(16)	67(5)
H(17C)	-3500(30)	760(30)	5405(18)	83(7)
H(22B)	4820(20)	6280(20)	6328(15)	59(5)
H(20B)	3300(30)	2880(20)	8530(18)	75(6)
H(18A)	-1820(30)	1180(30)	9640(20)	98(8)
H(18B)	60(30)	1260(20)	9650(18)	83(6)
H(18C)	-540(30)	2370(30)	10320(20)	93(7)
H(17B)	-4620(30)	1820(30)	5620(20)	110(9)
H(22C)	3180(30)	5230(20)	5897(19)	85(7)
H(17A)	-3330(30)	2070(20)	4978(19)	78(6)

4.4 Appendix 4: The structure of Cp1Cp2Fe, η^5-[1-(3,5-dimethylphenyl)-3-methyl-4,5,6,7-tetrahydro-2H-indenyl]-η^5-[1-(3,5-dimethylphenyl)-2-formyl-3-methyl-4,5,6,7-tetrahydro-2H-indenyl]iron(II)], as determined by X-ray crystallography

CIF: 00SRV121*

Space Group: P2(1)/n

Figure 18. The molecular structure of Cp1Cp2Fe



* H. Puschmann, C. Broder, Durham University Crystallography Department, 28.01.2000

4.4.1 Useful bond lengths, angles and torsion angles for Cp1Cp2Fe:

Complete crystallographic data for Cp1Cp2Fe is given in section 4.4.2. Presented here are a few bond lengths and angles which may be of interest as they pertain to major structural features.

Bond Lengths /Å

Fe-C101	2.0538(13)
Fe-C102	2.0424(14)
Fe-C103	2.0752(13)
Fe-C104	2.1006(13)
Fe-C109	2.1032(13)
Fe-C201	2.0785(13)
Fe-C202	2.0506(13)
Fe-C203	2.0801(13)
Fe-C204	2.0785(13)
Fe-C209	2.0852(13)

Angles /°

(Internal angle in flat regular pentagon = 108°)

C101-C102-C103	108.56(12)
C102-C103-C104	107.02(11)
C103-C104-C109	108.94(11)
C104-C109-C101	108.42(11)
C109-C101-C102	106.99(11)
C201-C202-C203	109.33(12)
C202-C203-C204	107.18(11)
C203-C204-C209	109.03(11)
C204-C209-C201	107.79(11)
C209-C201-C202	106.66(11)

Torsion Angles /°

C102-C101-C111-C112	-133.77(15)
C102-C101-C111-C116	47.33(19)
C109-C101-C111-C112	55.6(2)
C109-C101-C111-C116	-123.32(15)
C202-C201-C211-C212	-22.5(2)
C209-C201 C211-C212	153.23(13)
C202-C201-C211-C216	157.55(13)
C209-C201-C211-C216	-26.7(2)
O1-C1-C102-C103	14.7(3)

4.4.2 Complete crystallographic information for Cp1Cp2Fe (also refer to figure. 18, above)

CIF file for 00SRV121

Horst Pushmann and Charlie Broder, Durham University Crystallography, 28/01/2000

Table 1. Crystal data and structure refinement for 00SRV121.

Identification code	00SRV121	
Empirical formula	C37 H42 Fe O	
Formula weight	558.56	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.6281(2) Å	a= 90°.
	b = 24.0535(7) Å	b= 99.3990(10)°.
	c = 15.9949(5) Å	g = 90°.
Volume	2895.38(15) $Å^3$	
Z	4	
Density (calculated)	1.281 Mg/m^3	
Absorption coefficient	0.549 mm^{-1}	
F(000)	1192	
Crystal size	0.7 x 0.5 x 0.4 mm^3	
Theta range for data collection	1.54 to 30.45°.	
Index ranges	-10<=h<=10, -34<=k<=32, -22<=l<=22	
Reflections collected	36407	
Independent reflections	8171 [R(int) = 0.0240]	
Completeness to theta = 30.45°	92.9 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.807518 and 0.645544	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8171 / 0 / 358	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.0987	
R indices (all data)	R1 = 0.0421, wR2 = 0.1020	
Extinction coefficient	not refined	
Largest diff. peak and hole	1.365 and -0.358 $e.Å^{-3}$	

Table 3. Bond lengths [Å] and angles [°] for 00SRV121.

Fe(1)-C(102)	2.0424(14)
Fe(1)-C(202)	2.0506(13)
Fe(1)-C(101)	2.0538(13)
Fe(1)-C(103)	2.0752(13)
Fe(1)-C(204)	2.0785(13)
Fe(1)-C(201)	2.0785(13)
Fe(1)-C(203)	2.0801(13)
Fe(1)-C(209)	2.0852(13)
Fe(1)-C(104)	2.1006(13)
Fe(1)-C(109)	2.1032(13)
C(101)-C(109)	1.4292(18)
C(101)-C(102)	1.4528(18)
C(101)-C(111)	1.4793(18)
C(102)-C(103)	1.4395(19)
C(102)-C(1)	1.452(2)
C(103)-C(104)	1.4307(18)
C(103)-C(110)	1.5007(19)
C(104)-C(109)	1.4311(19)
C(104)-C(105)	1.5046(18)
C(105)-C(106)	1.534(2)
C(105)-H(10B)	0.9900
C(105)-H(10C)	0.9900
C(106)-C(107)	1.532(2)
C(106)-H(10D)	0.9900
C(106)-H(10E)	0.9900
C(107)-C(108)	1.538(2)
C(107)-H(10F)	0.9900
C(107)-H(10G)	0.9900
C(108)-C(109)	1.5052(18)
C(108)-H(10H)	0.9900
C(108)-H(10I)	0.9900
C(110)-H(11A)	0.9800
C(110)-H(11B)	0.9800
C(110)-H(11C)	0.9800
C(111)-C(112)	1.399(2)
C(111)-C(116)	1.3992(19)
C(112)-C(113)	1.399(2)
C(112)-H(11D)	0.9500
C(113)-C(114)	1.397(2)
C(113)-C(117)	1.512(2)
C(114)-C(115)	1.395(2)
C(114)-H(11E)	0.9500
C(115)-C(116)	1.395(2)
C(115)-C(118)	1.512(2)
C(116)-H(11F)	0.9500
C(117)-H(11G)	0.9800

C(117)-H(11H)	0.9800
C(117)-H(11I)	0.9800
C(118)-H(11J)	0.9800
C(118)-H(11K)	0.9800
C(118)-H(11L)	0.9800
C(201)-C(202)	1.4423(18)
C(201)-C(209)	1.4449(18)
C(201)-C(211)	1.4752(17)
C(202)-C(203)	1.4268(18)
C(202)-H(20A)	1.0000
C(203)-C(204)	1.4267(18)
C(203)-C(210)	1.4983(19)
C(204)-C(209)	1.4338(18)
C(204)-C(205)	1.5066(18)
C(205)-C(206)	1.532(2)
C(205)-H(20B)	0.9900
C(205)-H(20C)	0.9900
C(206)-C(207)	1.528(2)
C(206)-H(20D)	0.9900
C(206)-H(20E)	0.9900
C(207)-C(208)	1.5382(19)
C(207)-H(20F)	0.9900
C(207)-H(20G)	0.9900
C(208)-C(209)	1.5084(18)
C(208)-H(20H)	0.9900
C(208)-H(20I)	0.9900
C(210)-H(21A)	0.9800
C(210)-H(21B)	0.9800
C(210)-H(21C)	0.9800
C(211)-C(216)	1.4021(18)
C(211)-C(212)	1.4033(18)
C(212)-C(213)	1.3945(19)
C(212)-H(21D)	0.9500
C(213)-C(214)	1.397(2)
C(213)-C(217)	1.510(2)
C(214)-C(215)	1.394(2)
C(214)-H(21E)	0.9500
C(215)-C(216)	1.3982(18)
C(215)-C(218)	1.513(2)
C(216)-H(21F)	0.9500
C(217)-H(21G)	0.9800
C(217)-H(21H)	0.9800
C(217)-H(21I)	0.9800
C(218)-H(21J)	0.9800
C(218)-H(21K)	0.9800
C(218)-H(21L)	0.9800
O(1)-C(1)	1.221(2)
C(1)-H(1A)	0.9500

C(102)-Fe(1)-C(202)	120.46(6)
C(102)-Fe(1)-C(101)	41.55(5)
C(202)-Fe(1)-C(101)	107.56(5)
C(102)-Fe(1)-C(103)	40.91(5)
C(202)-Fe(1)-C(103)	155.29(5)
C(101)-Fe(1)-C(103)	69.32(5)
C(102)-Fe(1)-C(204)	124.83(5)
C(202)-Fe(1)-C(204)	67.58(5)
C(101)-Fe(1)-C(204)	162.30(5)
C(103)-Fe(1)-C(204)	107.54(5)
C(102)-Fe(1)-C(201)	155.90(5)
C(202)-Fe(1)-C(201)	40.88(5)
C(101)-Fe(1)-C(201)	120.28(5)
C(103)-Fe(1)-C(201)	162.05(5)
C(204)-Fe(1)-C(201)	68.04(5)
C(102)-Fe(1)-C(203)	107.16(5)
C(202)-Fe(1)-C(203)	40.41(5)
C(101)-Fe(1)-C(203)	125.24(5)
C(103)-Fe(1)-C(203)	120.15(5)
C(204)-Fe(1)-C(203)	40.13(5)
C(201)-Fe(1)-C(203)	68.50(5)
C(102)-Fe(1)-C(209)	161.72(5)
C(202)-Fe(1)-C(209)	68.10(5)
C(101)-Fe(1)-C(209)	155.61(5)
C(103)-Fe(1)-C(209)	124.90(5)
C(204)-Fe(1)-C(209)	40.29(5)
C(201)-Fe(1)-C(209)	40.61(5)
C(203)-Fe(1)-C(209)	68.00(5)
C(102)-Fe(1)-C(104)	67.68(5)
C(202)-Fe(1)-C(104)	163.24(5)
C(101)-Fe(1)-C(104)	67.92(5)
C(103)-Fe(1)-C(104)	40.07(5)
C(204)-Fe(1)-C(104)	121.60(5)
C(201)-Fe(1)-C(104)	126.14(5)
C(203)-Fe(1)-C(104)	155.38(5)
C(209)-Fe(1)-C(104)	108.92(5)
C(102)-Fe(1)-C(109)	67.93(5)
C(202)-Fe(1)-C(109)	126.54(5)
C(101)-Fe(1)-C(109)	40.20(5)
C(103)-Fe(1)-C(109)	67.75(5)
C(204)-Fe(1)-C(109)	156.18(5)
C(201)-Fe(1)-C(109)	108.81(5)
C(203)-Fe(1)-C(109)	162.78(5)
C(209)-Fe(1)-C(109)	121.82(5)
C(104)-Fe(1)-C(109)	39.81(5)
C(109)-C(101)-C(102)	106.99(11)
C(109)-C(101)-C(111)	126.67(12)

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C(102)-C(101)-C(111)  125.82(12)
C(109)-C(101)-Fe(1)    71.76(7)
C(102)-C(101)-Fe(1)    68.81(7)
C(111)-C(101)-Fe(1)   130.85(10)
C(103)-C(102)-C(1)    127.79(13)
C(103)-C(102)-C(101)  108.56(12)
C(1)-C(102)-C(101)    123.43(13)
C(103)-C(102)-Fe(1)    70.77(8)
C(1)-C(102)-Fe(1)     121.29(10)
C(101)-C(102)-Fe(1)    69.65(7)
C(104)-C(103)-C(102)  107.02(11)
C(104)-C(103)-C(110)  126.81(13)
C(102)-C(103)-C(110)  125.91(12)
C(104)-C(103)-Fe(1)    70.92(7)
C(102)-C(103)-Fe(1)    68.32(8)
C(110)-C(103)-Fe(1)   130.30(10)
C(103)-C(104)-C(109)  108.94(11)
C(103)-C(104)-C(105)  127.97(12)
C(109)-C(104)-C(105)  122.83(12)
C(103)-C(104)-Fe(1)    69.01(7)
C(109)-C(104)-Fe(1)    70.19(7)
C(105)-C(104)-Fe(1)   131.49(9)
C(104)-C(105)-C(106)  111.58(12)
C(104)-C(105)-H(10B)  109.3
C(106)-C(105)-H(10B)  109.3
C(104)-C(105)-H(10C)  109.3
C(106)-C(105)-H(10C)  109.3
H(10B)-C(105)-H(10C)  108.0
C(107)-C(106)-C(105)  111.98(12)
C(107)-C(106)-H(10D)  109.2
C(105)-C(106)-H(10D)  109.2
C(107)-C(106)-H(10E)  109.2
C(105)-C(106)-H(10E)  109.2
H(10D)-C(106)-H(10E)  107.9
C(106)-C(107)-C(108)  111.76(12)
C(106)-C(107)-H(10F)  109.3
C(108)-C(107)-H(10F)  109.3
C(106)-C(107)-H(10G)  109.3
C(108)-C(107)-H(10G)  109.3
H(10F)-C(107)-H(10G)  107.9
C(109)-C(108)-C(107)  109.73(12)
C(109)-C(108)-H(10H)  109.7
C(107)-C(108)-H(10H)  109.7
C(109)-C(108)-H(10I)  109.7
C(107)-C(108)-H(10I)  109.7
H(10H)-C(108)-H(10I)  108.2
C(101)-C(109)-C(104)  108.47(11)
C(101)-C(109)-C(108)  128.01(12)
```

C(104)-C(109)-C(108) 123.18(12)
C(101)-C(109)-Fe(1) 68.04(7)
C(104)-C(109)-Fe(1) 70.00(7)
C(108)-C(109)-Fe(1) 133.05(9)
C(103)-C(110)-H(11A) 109.5
C(103)-C(110)-H(11B) 109.5
H(11A)-C(110)-H(11B) 109.5
C(103)-C(110)-H(11C) 109.5
H(11A)-C(110)-H(11C) 109.5
H(11B)-C(110)-H(11C) 109.5
C(112)-C(111)-C(116) 118.85(13)
C(112)-C(111)-C(101) 122.26(12)
C(116)-C(111)-C(101) 118.88(13)
C(111)-C(112)-C(113) 120.83(13)
C(111)-C(112)-H(11D) 119.6
C(113)-C(112)-H(11D) 119.6
C(114)-C(113)-C(112) 118.88(14)
C(114)-C(113)-C(117) 120.78(14)
C(112)-C(113)-C(117) 120.34(14)
C(115)-C(114)-C(113) 121.43(14)
C(115)-C(114)-H(11E) 119.3
C(113)-C(114)-H(11E) 119.3
C(116)-C(115)-C(114) 118.58(13)
C(116)-C(115)-C(118) 119.97(15)
C(114)-C(115)-C(118) 121.44(14)
C(115)-C(116)-C(111) 121.38(14)
C(115)-C(116)-H(11F) 119.3
C(111)-C(116)-H(11F) 119.3
C(113)-C(117)-H(11G) 109.5
C(113)-C(117)-H(11H) 109.5
H(11G)-C(117)-H(11H) 109.5
C(113)-C(117)-H(11I) 109.5
H(11G)-C(117)-H(11I) 109.5
H(11H)-C(117)-H(11I) 109.5
C(115)-C(118)-H(11J) 109.5
C(115)-C(118)-H(11K) 109.5
H(11J)-C(118)-H(11K) 109.5
C(115)-C(118)-H(11L) 109.5
H(11J)-C(118)-H(11L) 109.5
H(11K)-C(118)-H(11L) 109.5
C(202)-C(201)-C(209) 106.66(11)
C(202)-C(201)-C(211) 124.63(12)
C(209)-C(201)-C(211) 128.60(12)
C(202)-C(201)-Fe(1) 68.52(7)
C(209)-C(201)-Fe(1) 69.94(7)
C(211)-C(201)-Fe(1) 129.20(9)
C(203)-C(202)-C(201) 109.33(12)
C(203)-C(202)-Fe(1) 70.91(8)

C(201)-C(202)-Fe(1) 70.60(7)
C(203)-C(202)-H(20A) 125.3
C(201)-C(202)-H(20A) 125.3
Fe(1)-C(202)-H(20A) 125.3
C(204)-C(203)-C(202) 107.18(11)
C(204)-C(203)-C(210) 126.21(12)
C(202)-C(203)-C(210) 126.45(12)
C(204)-C(203)-Fe(1) 69.87(7)
C(202)-C(203)-Fe(1) 68.68(7)
C(210)-C(203)-Fe(1) 130.05(10)
C(203)-C(204)-C(209) 109.03(11)
C(203)-C(204)-C(205) 127.80(12)
C(209)-C(204)-C(205) 123.04(12)
C(203)-C(204)-Fe(1) 70.00(7)
C(209)-C(204)-Fe(1) 70.11(7)
C(205)-C(204)-Fe(1) 129.19(9)
C(204)-C(205)-C(206) 110.51(11)
C(204)-C(205)-H(20B) 109.5
C(206)-C(205)-H(20B) 109.5
C(204)-C(205)-H(20C) 109.5
C(206)-C(205)-H(20C) 109.5
H(20B)-C(205)-H(20C) 108.1
C(207)-C(206)-C(205) 110.89(12)
C(207)-C(206)-H(20D) 109.5
C(205)-C(206)-H(20D) 109.5
C(207)-C(206)-H(20E) 109.5
C(205)-C(206)-H(20E) 109.5
H(20D)-C(206)-H(20E) 108.0
C(206)-C(207)-C(208) 111.13(11)
C(206)-C(207)-H(20F) 109.4
C(208)-C(207)-H(20F) 109.4
C(206)-C(207)-H(20G) 109.4
C(208)-C(207)-H(20G) 109.4
H(20F)-C(207)-H(20G) 108.0
C(209)-C(208)-C(207) 110.65(11)
C(209)-C(208)-H(20H) 109.5
C(207)-C(208)-H(20H) 109.5
C(209)-C(208)-H(20I) 109.5
C(207)-C(208)-H(20I) 109.5
H(20H)-C(208)-H(20I) 108.1
C(204)-C(209)-C(201) 107.79(11)
C(204)-C(209)-C(208) 122.30(12)
C(201)-C(209)-C(208) 129.59(12)
C(204)-C(209)-Fe(1) 69.61(7)
C(201)-C(209)-Fe(1) 69.45(7)
C(208)-C(209)-Fe(1) 131.29(9)
C(203)-C(210)-H(21A) 109.5
C(203)-C(210)-H(21B) 109.5

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H(21A)-C(210)-H(21B) 109.5
C(203)-C(210)-H(21C) 109.5
H(21A)-C(210)-H(21C) 109.5
H(21B)-C(210)-H(21C) 109.5
C(216)-C(211)-C(212) 117.81(12)
C(216)-C(211)-C(201) 122.91(12)
C(212)-C(211)-C(201) 119.29(12)
C(213)-C(212)-C(211) 121.65(13)
C(213)-C(212)-H(21D) 119.2
C(211)-C(212)-H(21D) 119.2
C(212)-C(213)-C(214) 119.00(13)
C(212)-C(213)-C(217) 119.93(14)
C(214)-C(213)-C(217) 121.06(13)
C(215)-C(214)-C(213) 120.92(13)
C(215)-C(214)-H(21E) 119.5
C(213)-C(214)-H(21E) 119.5
C(214)-C(215)-C(216) 119.01(13)
C(214)-C(215)-C(218) 120.99(13)
C(216)-C(215)-C(218) 119.99(13)
C(215)-C(216)-C(211) 121.58(13)
C(215)-C(216)-H(21F) 119.2
C(211)-C(216)-H(21F) 119.2
C(213)-C(217)-H(21G) 109.5
C(213)-C(217)-H(21H) 109.5
H(21G)-C(217)-H(21H) 109.5
C(213)-C(217)-H(21I) 109.5
H(21G)-C(217)-H(21I) 109.5
H(21H)-C(217)-H(21I) 109.5
C(215)-C(218)-H(21J) 109.5
C(215)-C(218)-H(21K) 109.5
H(21J)-C(218)-H(21K) 109.5
C(215)-C(218)-H(21L) 109.5
H(21J)-C(218)-H(21L) 109.5
H(21K)-C(218)-H(21L) 109.5
O(1)-C(1)-C(102)     126.27(16)
O(1)-C(1)-H(1A)      116.9
C(102)-C(1)-H(1A)    116.9
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Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for 00SRV121. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	19(1)	15(1)	17(1)	2(1)	2(1)	0(1)
C(101)	21(1)	19(1)	20(1)	1(1)	0(1)	-3(1)
C(102)	22(1)	22(1)	19(1)	2(1)	0(1)	-1(1)
C(103)	20(1)	21(1)	22(1)	2(1)	2(1)	1(1)
C(104)	19(1)	21(1)	20(1)	0(1)	3(1)	-1(1)
C(105)	24(1)	25(1)	22(1)	-3(1)	5(1)	2(1)
C(106)	28(1)	30(1)	20(1)	-2(1)	3(1)	1(1)
C(107)	30(1)	35(1)	22(1)	4(1)	7(1)	-4(1)
C(108)	25(1)	24(1)	21(1)	5(1)	1(1)	-6(1)
C(109)	20(1)	21(1)	19(1)	2(1)	2(1)	-3(1)
C(110)	28(1)	23(1)	32(1)	4(1)	2(1)	6(1)
C(111)	27(1)	20(1)	19(1)	1(1)	3(1)	-5(1)
C(112)	28(1)	21(1)	24(1)	2(1)	1(1)	-5(1)
C(113)	35(1)	21(1)	24(1)	3(1)	6(1)	-3(1)
C(114)	40(1)	21(1)	25(1)	-2(1)	8(1)	-8(1)
C(115)	31(1)	28(1)	22(1)	-3(1)	5(1)	-11(1)
C(116)	26(1)	25(1)	23(1)	-1(1)	3(1)	-5(1)
C(117)	46(1)	24(1)	40(1)	4(1)	6(1)	4(1)
C(118)	36(1)	38(1)	37(1)	-9(1)	1(1)	-13(1)
C(201)	20(1)	18(1)	21(1)	2(1)	4(1)	2(1)
C(202)	25(1)	19(1)	20(1)	1(1)	6(1)	2(1)
C(203)	25(1)	21(1)	18(1)	1(1)	5(1)	-1(1)
C(204)	21(1)	18(1)	19(1)	2(1)	4(1)	-1(1)
C(205)	28(1)	18(1)	24(1)	4(1)	4(1)	-2(1)
C(206)	32(1)	18(1)	28(1)	0(1)	5(1)	0(1)
C(207)	30(1)	22(1)	28(1)	-2(1)	2(1)	-7(1)
C(208)	23(1)	21(1)	21(1)	-1(1)	1(1)	-3(1)
C(209)	20(1)	19(1)	19(1)	1(1)	3(1)	0(1)
C(210)	41(1)	27(1)	18(1)	1(1)	6(1)	-4(1)
C(211)	18(1)	19(1)	22(1)	3(1)	3(1)	2(1)
C(212)	24(1)	23(1)	24(1)	3(1)	6(1)	4(1)
C(213)	27(1)	22(1)	30(1)	4(1)	6(1)	6(1)
C(214)	29(1)	24(1)	26(1)	7(1)	2(1)	3(1)
C(215)	23(1)	26(1)	22(1)	3(1)	2(1)	0(1)
C(216)	21(1)	21(1)	22(1)	1(1)	2(1)	2(1)
C(217)	49(1)	26(1)	38(1)	6(1)	10(1)	17(1)
C(218)	41(1)	37(1)	21(1)	3(1)	3(1)	4(1)
O(1)	56(1)	46(1)	28(1)	11(1)	-1(1)	7(1)
C(1)	31(1)	33(1)	23(1)	2(1)	0(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for 00SRV121.

	x	y	z	U(eq)
H(10B)	7684	2389	6344	28
H(10C)	9694	2541	6263	28
H(10D)	8112	2847	5009	31
H(10E)	6552	3094	5458	31
H(10F)	8350	3819	5012	34
H(10G)	10041	3576	5630	34
H(10H)	9013	4311	6364	28
H(10I)	6999	4096	6151	28
H(11A)	10875	2231	8363	41
H(11B)	9044	2017	7827	41
H(11C)	9115	2214	8787	41
H(11D)	6634	4702	7603	30
H(11E)	9585	5900	8950	34
H(11F)	11503	4334	8915	30
H(11G)	5227	5582	7972	55
H(11H)	6464	5941	7459	55
H(11I)	6445	6067	8440	55
H(11J)	12908	5683	9370	56
H(11K)	13455	5044	9522	56
H(11L)	12346	5352	10153	56
H(20A)	4770	4081	8510	26
H(20B)	3963	2016	8580	28
H(20C)	6086	2055	8691	28
H(20D)	6084	1856	7273	31
H(20E)	4774	1409	7583	31
H(20F)	2290	1993	7015	32
H(20G)	3333	1763	6294	32
H(20H)	4702	2614	6170	26
H(20I)	2656	2760	6182	26
H(21A)	4405	3067	9895	43
H(21B)	6049	3482	9911	43
H(21C)	6326	2828	9812	43
H(21D)	2825	4564	7505	28
H(21E)	2128	5084	5066	32
H(21F)	4151	3554	5679	26
H(21G)	593	5559	6149	56
H(21H)	2488	5728	6673	56
H(21I)	1111	5382	7123	56
H(21J)	4550	4029	4305	50
H(21K)	3337	4560	4018	50
H(21L)	2443	3960	4052	50
H(1A)	9404	3728	9654	35

Table 6. Torsion angles [°] for 00SRV121.

C(102)-Fe(1)-C(101)-C(109)	117.24(11)
C(202)-Fe(1)-C(101)-C(109)	-126.37(8)
C(103)-Fe(1)-C(101)-C(109)	79.60(8)
C(204)-Fe(1)-C(101)-C(109)	162.53(15)
C(201)-Fe(1)-C(101)-C(109)	-83.55(9)
C(203)-Fe(1)-C(101)-C(109)	-167.40(8)
C(209)-Fe(1)-C(101)-C(109)	-50.81(16)
C(104)-Fe(1)-C(101)-C(109)	36.46(8)
C(202)-Fe(1)-C(101)-C(102)	116.39(8)
C(103)-Fe(1)-C(101)-C(102)	-37.63(8)
C(204)-Fe(1)-C(101)-C(102)	45.3(2)
C(201)-Fe(1)-C(101)-C(102)	159.21(8)
C(203)-Fe(1)-C(101)-C(102)	75.36(9)
C(209)-Fe(1)-C(101)-C(102)	-168.05(11)
C(104)-Fe(1)-C(101)-C(102)	-80.78(8)
C(109)-Fe(1)-C(101)-C(102)	-117.24(11)
C(102)-Fe(1)-C(101)-C(111)	-119.64(15)
C(202)-Fe(1)-C(101)-C(111)	-3.25(13)
C(103)-Fe(1)-C(101)-C(111)	-157.28(13)
C(204)-Fe(1)-C(101)-C(111)	-74.4(2)
C(201)-Fe(1)-C(101)-C(111)	39.57(14)
C(203)-Fe(1)-C(101)-C(111)	-44.29(14)
C(209)-Fe(1)-C(101)-C(111)	72.31(18)
C(104)-Fe(1)-C(101)-C(111)	159.57(14)
C(109)-Fe(1)-C(101)-C(111)	123.12(15)
C(109)-C(101)-C(102)-C(103)	-1.68(15)
C(111)-C(101)-C(102)-C(103)	-173.85(12)
Fe(1)-C(101)-C(102)-C(103)	60.32(9)
C(109)-C(101)-C(102)-C(1)	-176.77(13)
C(111)-C(101)-C(102)-C(1)	11.1(2)
Fe(1)-C(101)-C(102)-C(1)	-114.77(14)
C(109)-C(101)-C(102)-Fe(1)	-62.00(9)
C(111)-C(101)-C(102)-Fe(1)	125.83(14)
C(202)-Fe(1)-C(102)-C(103)	158.53(8)
C(101)-Fe(1)-C(102)-C(103)	-119.28(11)
C(204)-Fe(1)-C(102)-C(103)	75.99(9)
C(201)-Fe(1)-C(102)-C(103)	-167.91(11)
C(203)-Fe(1)-C(102)-C(103)	116.51(8)
C(209)-Fe(1)-C(102)-C(103)	44.9(2)
C(104)-Fe(1)-C(102)-C(103)	-37.87(8)
C(109)-Fe(1)-C(102)-C(103)	-81.02(8)
C(202)-Fe(1)-C(102)-C(1)	35.34(14)
C(101)-Fe(1)-C(102)-C(1)	117.53(15)
C(103)-Fe(1)-C(102)-C(1)	-123.19(15)
C(204)-Fe(1)-C(102)-C(1)	-47.21(14)
C(201)-Fe(1)-C(102)-C(1)	68.89(18)

C(203)-Fe(1)-C(102)-C(1)	-6.68(13)
C(209)-Fe(1)-C(102)-C(1)	-78.3(2)
C(104)-Fe(1)-C(102)-C(1)	-161.06(13)
C(109)-Fe(1)-C(102)-C(1)	155.79(13)
C(202)-Fe(1)-C(102)-C(101)	-82.20(9)
C(103)-Fe(1)-C(102)-C(101)	119.28(11)
C(204)-Fe(1)-C(102)-C(101)	-164.74(8)
C(201)-Fe(1)-C(102)-C(101)	-48.64(16)
C(203)-Fe(1)-C(102)-C(101)	-124.21(8)
C(209)-Fe(1)-C(102)-C(101)	164.18(15)
C(104)-Fe(1)-C(102)-C(101)	81.41(8)
C(109)-Fe(1)-C(102)-C(101)	38.26(8)
C(1)-C(102)-C(103)-C(104)	175.87(14)
C(101)-C(102)-C(103)-C(104)	1.06(15)
Fe(1)-C(102)-C(103)-C(104)	60.69(9)
C(1)-C(102)-C(103)-C(110)	-9.7(2)
C(101)-C(102)-C(103)-C(110)	175.53(13)
Fe(1)-C(102)-C(103)-C(110)	-124.85(14)
C(1)-C(102)-C(103)-Fe(1)	115.19(15)
C(101)-C(102)-C(103)-Fe(1)	-59.62(9)
C(102)-Fe(1)-C(103)-C(104)	-118.09(11)
C(202)-Fe(1)-C(103)-C(104)	-167.10(12)
C(101)-Fe(1)-C(103)-C(104)	-79.89(8)
C(204)-Fe(1)-C(103)-C(104)	118.55(8)
C(201)-Fe(1)-C(103)-C(104)	45.8(2)
C(203)-Fe(1)-C(103)-C(104)	160.50(8)
C(209)-Fe(1)-C(103)-C(104)	77.57(9)
C(109)-Fe(1)-C(103)-C(104)	-36.59(8)
C(202)-Fe(1)-C(103)-C(102)	-49.01(16)
C(101)-Fe(1)-C(103)-C(102)	38.20(8)
C(204)-Fe(1)-C(103)-C(102)	-123.36(8)
C(201)-Fe(1)-C(103)-C(102)	163.89(15)
C(203)-Fe(1)-C(103)-C(102)	-81.41(9)
C(209)-Fe(1)-C(103)-C(102)	-164.34(8)
C(104)-Fe(1)-C(103)-C(102)	118.09(11)
C(109)-Fe(1)-C(103)-C(102)	81.50(8)
C(102)-Fe(1)-C(103)-C(110)	119.37(16)
C(202)-Fe(1)-C(103)-C(110)	70.36(19)
C(101)-Fe(1)-C(103)-C(110)	157.57(14)
C(204)-Fe(1)-C(103)-C(110)	-3.99(14)
C(201)-Fe(1)-C(103)-C(110)	-76.7(2)
C(203)-Fe(1)-C(103)-C(110)	37.96(15)
C(209)-Fe(1)-C(103)-C(110)	-44.97(15)
C(104)-Fe(1)-C(103)-C(110)	-122.54(16)
C(109)-Fe(1)-C(103)-C(110)	-159.12(14)
C(102)-C(103)-C(104)-C(109)	-0.04(15)
C(110)-C(103)-C(104)-C(109)	-174.44(13)
Fe(1)-C(103)-C(104)-C(109)	58.98(9)

C(102)-C(103)-C(104)-C(105)	174.06(13)
C(110)-C(103)-C(104)-C(105)	-0.3(2)
Fe(1)-C(103)-C(104)-C(105)	-126.92(14)
C(102)-C(103)-C(104)-Fe(1)	-59.02(9)
C(110)-C(103)-C(104)-Fe(1)	126.58(14)
C(102)-Fe(1)-C(104)-C(103)	38.65(8)
C(202)-Fe(1)-C(104)-C(103)	161.12(17)
C(101)-Fe(1)-C(104)-C(103)	83.70(8)
C(204)-Fe(1)-C(104)-C(103)	-79.53(9)
C(201)-Fe(1)-C(104)-C(103)	-164.12(8)
C(203)-Fe(1)-C(104)-C(103)	-43.84(16)
C(209)-Fe(1)-C(104)-C(103)	-122.15(8)
C(109)-Fe(1)-C(104)-C(103)	120.50(11)
C(102)-Fe(1)-C(104)-C(109)	-81.85(8)
C(202)-Fe(1)-C(104)-C(109)	40.6(2)
C(101)-Fe(1)-C(104)-C(109)	-36.80(7)
C(103)-Fe(1)-C(104)-C(109)	-120.50(11)
C(204)-Fe(1)-C(104)-C(109)	159.97(7)
C(201)-Fe(1)-C(104)-C(109)	75.38(9)
C(203)-Fe(1)-C(104)-C(109)	-164.34(11)
C(209)-Fe(1)-C(104)-C(109)	117.35(8)
C(102)-Fe(1)-C(104)-C(105)	161.36(14)
C(202)-Fe(1)-C(104)-C(105)	-76.2(2)
C(101)-Fe(1)-C(104)-C(105)	-153.59(14)
C(103)-Fe(1)-C(104)-C(105)	122.71(16)
C(204)-Fe(1)-C(104)-C(105)	43.18(14)
C(201)-Fe(1)-C(104)-C(105)	-41.41(15)
C(203)-Fe(1)-C(104)-C(105)	78.87(18)
C(209)-Fe(1)-C(104)-C(105)	0.57(14)
C(109)-Fe(1)-C(104)-C(105)	-116.79(15)
C(103)-C(104)-C(105)-C(106)	176.12(13)
C(109)-C(104)-C(105)-C(106)	-10.53(18)
Fe(1)-C(104)-C(105)-C(106)	81.31(15)
C(104)-C(105)-C(106)-C(107)	41.99(16)
C(105)-C(106)-C(107)-C(108)	-63.79(16)
C(106)-C(107)-C(108)-C(109)	48.66(16)
C(102)-C(101)-C(109)-C(104)	1.65(14)
C(111)-C(101)-C(109)-C(104)	173.73(13)
Fe(1)-C(101)-C(109)-C(104)	-58.44(9)
C(102)-C(101)-C(109)-C(108)	-171.66(13)
C(111)-C(101)-C(109)-C(108)	0.4(2)
Fe(1)-C(101)-C(109)-C(108)	128.25(14)
C(102)-C(101)-C(109)-Fe(1)	60.09(9)
C(111)-C(101)-C(109)-Fe(1)	-127.83(14)
C(103)-C(104)-C(109)-C(101)	-1.02(15)
C(105)-C(104)-C(109)-C(101)	-175.48(12)
Fe(1)-C(104)-C(109)-C(101)	57.25(9)
C(103)-C(104)-C(109)-C(108)	172.69(12)

C(105)-C(104)-C(109)-C(108)	-1.8(2)
Fe(1)-C(104)-C(109)-C(108)	-129.05(12)
C(103)-C(104)-C(109)-Fe(1)	-58.26(9)
C(105)-C(104)-C(109)-Fe(1)	127.27(12)
C(107)-C(108)-C(109)-C(101)	155.16(13)
C(107)-C(108)-C(109)-C(104)	-17.26(17)
C(107)-C(108)-C(109)-Fe(1)	-110.21(14)
C(102)-Fe(1)-C(109)-C(101)	-39.52(8)
C(202)-Fe(1)-C(109)-C(101)	72.84(9)
C(103)-Fe(1)-C(109)-C(101)	-83.86(8)
C(204)-Fe(1)-C(109)-C(101)	-166.94(12)
C(201)-Fe(1)-C(109)-C(101)	114.97(8)
C(203)-Fe(1)-C(109)-C(101)	37.0(2)
C(209)-Fe(1)-C(109)-C(101)	157.88(8)
C(104)-Fe(1)-C(109)-C(101)	-120.68(11)
C(102)-Fe(1)-C(109)-C(104)	81.16(8)
C(202)-Fe(1)-C(109)-C(104)	-166.48(8)
C(101)-Fe(1)-C(109)-C(104)	120.68(11)
C(103)-Fe(1)-C(109)-C(104)	36.82(7)
C(204)-Fe(1)-C(109)-C(104)	-46.26(16)
C(201)-Fe(1)-C(109)-C(104)	-124.36(8)
C(203)-Fe(1)-C(109)-C(104)	157.67(16)
C(209)-Fe(1)-C(109)-C(104)	-81.45(8)
C(102)-Fe(1)-C(109)-C(108)	-161.65(15)
C(202)-Fe(1)-C(109)-C(108)	-49.29(15)
C(101)-Fe(1)-C(109)-C(108)	-122.14(16)
C(103)-Fe(1)-C(109)-C(108)	154.01(15)
C(204)-Fe(1)-C(109)-C(108)	70.9(2)
C(201)-Fe(1)-C(109)-C(108)	-7.17(14)
C(203)-Fe(1)-C(109)-C(108)	-85.1(2)
C(209)-Fe(1)-C(109)-C(108)	35.74(15)
C(104)-Fe(1)-C(109)-C(108)	117.19(16)
C(109)-C(101)-C(111)-C(112)	55.6(2)
C(102)-C(101)-C(111)-C(112)	-133.77(15)
Fe(1)-C(101)-C(111)-C(112)	-41.77(19)
C(109)-C(101)-C(111)-C(116)	-123.32(15)
C(102)-C(101)-C(111)-C(116)	47.33(19)
Fe(1)-C(101)-C(111)-C(116)	139.33(12)
C(116)-C(111)-C(112)-C(113)	-1.8(2)
C(101)-C(111)-C(112)-C(113)	179.25(13)
C(111)-C(112)-C(113)-C(114)	2.4(2)
C(111)-C(112)-C(113)-C(117)	-177.03(14)
C(112)-C(113)-C(114)-C(115)	-1.1(2)
C(117)-C(113)-C(114)-C(115)	178.26(14)
C(113)-C(114)-C(115)-C(116)	-0.6(2)
C(113)-C(114)-C(115)-C(118)	179.48(14)
C(114)-C(115)-C(116)-C(111)	1.1(2)
C(118)-C(115)-C(116)-C(111)	-178.95(14)

C(112)-C(111)-C(116)-C(115)	0.1(2)
C(101)-C(111)-C(116)-C(115)	179.02(13)
C(102)-Fe(1)-C(201)-C(202)	-46.72(16)
C(101)-Fe(1)-C(201)-C(202)	-81.92(9)
C(103)-Fe(1)-C(201)-C(202)	159.70(15)
C(204)-Fe(1)-C(201)-C(202)	80.65(8)
C(203)-Fe(1)-C(201)-C(202)	37.30(8)
C(209)-Fe(1)-C(201)-C(202)	118.14(10)
C(104)-Fe(1)-C(201)-C(202)	-165.45(8)
C(109)-Fe(1)-C(201)-C(202)	-124.57(8)
C(102)-Fe(1)-C(201)-C(209)	-164.86(12)
C(202)-Fe(1)-C(201)-C(209)	-118.14(10)
C(101)-Fe(1)-C(201)-C(209)	159.94(7)
C(103)-Fe(1)-C(201)-C(209)	41.56(19)
C(204)-Fe(1)-C(201)-C(209)	-37.50(7)
C(203)-Fe(1)-C(201)-C(209)	-80.84(8)
C(104)-Fe(1)-C(201)-C(209)	76.41(9)
C(109)-Fe(1)-C(201)-C(209)	117.29(8)
C(102)-Fe(1)-C(201)-C(211)	71.13(19)
C(202)-Fe(1)-C(201)-C(211)	117.85(15)
C(101)-Fe(1)-C(201)-C(211)	35.93(14)
C(103)-Fe(1)-C(201)-C(211)	-82.4(2)
C(204)-Fe(1)-C(201)-C(211)	-161.50(13)
C(203)-Fe(1)-C(201)-C(211)	155.15(13)
C(209)-Fe(1)-C(201)-C(211)	-124.01(15)
C(104)-Fe(1)-C(201)-C(211)	-47.60(14)
C(109)-Fe(1)-C(201)-C(211)	-6.72(13)
C(209)-C(201)-C(202)-C(203)	-0.76(15)
C(211)-C(201)-C(202)-C(203)	175.79(12)
Fe(1)-C(201)-C(202)-C(203)	-60.60(10)
C(209)-C(201)-C(202)-Fe(1)	59.84(8)
C(211)-C(201)-C(202)-Fe(1)	-123.62(13)
C(102)-Fe(1)-C(202)-C(203)	-80.62(9)
C(101)-Fe(1)-C(202)-C(203)	-124.19(8)
C(103)-Fe(1)-C(202)-C(203)	-45.62(16)
C(204)-Fe(1)-C(202)-C(203)	37.69(8)
C(201)-Fe(1)-C(202)-C(203)	119.56(11)
C(209)-Fe(1)-C(202)-C(203)	81.34(8)
C(104)-Fe(1)-C(202)-C(203)	164.26(16)
C(109)-Fe(1)-C(202)-C(203)	-164.49(8)
C(102)-Fe(1)-C(202)-C(201)	159.83(7)
C(101)-Fe(1)-C(202)-C(201)	116.26(8)
C(103)-Fe(1)-C(202)-C(201)	-165.18(11)
C(204)-Fe(1)-C(202)-C(201)	-81.87(8)
C(203)-Fe(1)-C(202)-C(201)	-119.56(11)
C(209)-Fe(1)-C(202)-C(201)	-38.22(7)
C(104)-Fe(1)-C(202)-C(201)	44.7(2)
C(109)-Fe(1)-C(202)-C(201)	75.95(9)

C(201)-C(202)-C(203)-C(204)	0.89(15)
Fe(1)-C(202)-C(203)-C(204)	-59.52(9)
C(201)-C(202)-C(203)-C(210)	-174.81(13)
Fe(1)-C(202)-C(203)-C(210)	124.79(15)
C(201)-C(202)-C(203)-Fe(1)	60.40(9)
C(102)-Fe(1)-C(203)-C(204)	-124.14(8)
C(202)-Fe(1)-C(203)-C(204)	118.74(11)
C(101)-Fe(1)-C(203)-C(204)	-166.33(8)
C(103)-Fe(1)-C(203)-C(204)	-81.48(9)
C(201)-Fe(1)-C(203)-C(204)	81.01(8)
C(209)-Fe(1)-C(203)-C(204)	37.13(7)
C(104)-Fe(1)-C(203)-C(204)	-50.44(16)
C(109)-Fe(1)-C(203)-C(204)	165.27(16)
C(102)-Fe(1)-C(203)-C(202)	117.12(8)
C(101)-Fe(1)-C(203)-C(202)	74.93(10)
C(103)-Fe(1)-C(203)-C(202)	159.79(8)
C(204)-Fe(1)-C(203)-C(202)	-118.74(11)
C(201)-Fe(1)-C(203)-C(202)	-37.73(8)
C(209)-Fe(1)-C(203)-C(202)	-81.60(8)
C(104)-Fe(1)-C(203)-C(202)	-169.17(11)
C(109)-Fe(1)-C(203)-C(202)	46.5(2)
C(102)-Fe(1)-C(203)-C(210)	-3.22(14)
C(202)-Fe(1)-C(203)-C(210)	-120.34(16)
C(101)-Fe(1)-C(203)-C(210)	-45.41(15)
C(103)-Fe(1)-C(203)-C(210)	39.45(15)
C(204)-Fe(1)-C(203)-C(210)	120.93(16)
C(201)-Fe(1)-C(203)-C(210)	-158.07(14)
C(209)-Fe(1)-C(203)-C(210)	158.06(14)
C(104)-Fe(1)-C(203)-C(210)	70.49(19)
C(109)-Fe(1)-C(203)-C(210)	-73.8(2)
C(202)-C(203)-C(204)-C(209)	-0.67(15)
C(210)-C(203)-C(204)-C(209)	175.04(13)
Fe(1)-C(203)-C(204)-C(209)	-59.43(9)
C(202)-C(203)-C(204)-C(205)	-176.57(13)
C(210)-C(203)-C(204)-C(205)	-0.9(2)
Fe(1)-C(203)-C(204)-C(205)	124.67(14)
C(202)-C(203)-C(204)-Fe(1)	58.76(9)
C(210)-C(203)-C(204)-Fe(1)	-125.53(15)
C(102)-Fe(1)-C(204)-C(203)	74.46(9)
C(202)-Fe(1)-C(204)-C(203)	-37.94(8)
C(101)-Fe(1)-C(204)-C(203)	39.4(2)
C(103)-Fe(1)-C(204)-C(203)	116.25(8)
C(201)-Fe(1)-C(204)-C(203)	-82.25(8)
C(209)-Fe(1)-C(204)-C(203)	-120.04(11)
C(104)-Fe(1)-C(204)-C(203)	157.84(8)
C(109)-Fe(1)-C(204)-C(203)	-169.26(12)
C(102)-Fe(1)-C(204)-C(209)	-165.50(8)
C(202)-Fe(1)-C(204)-C(209)	82.10(8)

C(101)-Fe(1)-C(204)-C(209)	159.45(16)
C(103)-Fe(1)-C(204)-C(209)	-123.71(8)
C(201)-Fe(1)-C(204)-C(209)	37.79(7)
C(203)-Fe(1)-C(204)-C(209)	120.04(11)
C(104)-Fe(1)-C(204)-C(209)	-82.11(9)
C(109)-Fe(1)-C(204)-C(209)	-49.22(16)
C(102)-Fe(1)-C(204)-C(205)	-48.56(14)
C(202)-Fe(1)-C(204)-C(205)	-160.96(13)
C(101)-Fe(1)-C(204)-C(205)	-83.6(2)
C(103)-Fe(1)-C(204)-C(205)	-6.77(13)
C(201)-Fe(1)-C(204)-C(205)	154.73(13)
C(203)-Fe(1)-C(204)-C(205)	-123.02(15)
C(209)-Fe(1)-C(204)-C(205)	116.94(15)
C(104)-Fe(1)-C(204)-C(205)	34.83(14)
C(109)-Fe(1)-C(204)-C(205)	67.72(19)
C(203)-C(204)-C(205)-C(206)	-170.00(13)
C(209)-C(204)-C(205)-C(206)	14.62(18)
Fe(1)-C(204)-C(205)-C(206)	-75.75(15)
C(204)-C(205)-C(206)-C(207)	-47.51(16)
C(205)-C(206)-C(207)-C(208)	66.42(15)
C(206)-C(207)-C(208)-C(209)	-46.93(16)
C(203)-C(204)-C(209)-C(201)	0.21(14)
C(205)-C(204)-C(209)-C(201)	176.34(12)
Fe(1)-C(204)-C(209)-C(201)	-59.16(9)
C(203)-C(204)-C(209)-C(208)	-173.92(12)
C(205)-C(204)-C(209)-C(208)	2.2(2)
Fe(1)-C(204)-C(209)-C(208)	126.71(12)
C(203)-C(204)-C(209)-Fe(1)	59.37(9)
C(205)-C(204)-C(209)-Fe(1)	-124.50(13)
C(202)-C(201)-C(209)-C(204)	0.33(14)
C(211)-C(201)-C(209)-C(204)	-176.03(13)
Fe(1)-C(201)-C(209)-C(204)	59.26(9)
C(202)-C(201)-C(209)-C(208)	173.89(13)
C(211)-C(201)-C(209)-C(208)	-2.5(2)
Fe(1)-C(201)-C(209)-C(208)	-127.18(14)
C(202)-C(201)-C(209)-Fe(1)	-58.92(9)
C(211)-C(201)-C(209)-Fe(1)	124.71(13)
C(207)-C(208)-C(209)-C(204)	13.93(17)
C(207)-C(208)-C(209)-C(201)	-158.81(13)
C(207)-C(208)-C(209)-Fe(1)	104.30(13)
C(102)-Fe(1)-C(209)-C(204)	40.9(2)
C(202)-Fe(1)-C(209)-C(204)	-80.71(8)
C(101)-Fe(1)-C(209)-C(204)	-165.02(12)
C(103)-Fe(1)-C(209)-C(204)	75.26(9)
C(201)-Fe(1)-C(209)-C(204)	-119.18(10)
C(203)-Fe(1)-C(209)-C(204)	-36.99(7)
C(104)-Fe(1)-C(209)-C(204)	116.90(8)
C(109)-Fe(1)-C(209)-C(204)	158.91(8)

C(102)-Fe(1)-C(209)-C(201)	160.12(16)
C(202)-Fe(1)-C(209)-C(201)	38.46(7)
C(101)-Fe(1)-C(209)-C(201)	-45.84(15)
C(103)-Fe(1)-C(209)-C(201)	-165.57(7)
C(204)-Fe(1)-C(209)-C(201)	119.18(10)
C(203)-Fe(1)-C(209)-C(201)	82.19(8)
C(104)-Fe(1)-C(209)-C(201)	-123.92(7)
C(109)-Fe(1)-C(209)-C(201)	-81.91(8)
C(102)-Fe(1)-C(209)-C(208)	-74.7(2)
C(202)-Fe(1)-C(209)-C(208)	163.68(13)
C(101)-Fe(1)-C(209)-C(208)	79.37(18)
C(103)-Fe(1)-C(209)-C(208)	-40.35(14)
C(204)-Fe(1)-C(209)-C(208)	-115.61(15)
C(201)-Fe(1)-C(209)-C(208)	125.21(15)
C(203)-Fe(1)-C(209)-C(208)	-152.60(14)
C(104)-Fe(1)-C(209)-C(208)	1.29(13)
C(109)-Fe(1)-C(209)-C(208)	43.30(14)
C(202)-C(201)-C(211)-C(216)	157.55(13)
C(209)-C(201)-C(211)-C(216)	-26.7(2)
Fe(1)-C(201)-C(211)-C(216)	68.18(17)
C(202)-C(201)-C(211)-C(212)	-22.5(2)
C(209)-C(201)-C(211)-C(212)	153.23(13)
Fe(1)-C(201)-C(211)-C(212)	-111.91(13)
C(216)-C(211)-C(212)-C(213)	-0.5(2)
C(201)-C(211)-C(212)-C(213)	179.58(13)
C(211)-C(212)-C(213)-C(214)	-0.7(2)
C(211)-C(212)-C(213)-C(217)	178.61(14)
C(212)-C(213)-C(214)-C(215)	0.7(2)
C(217)-C(213)-C(214)-C(215)	-178.62(15)
C(213)-C(214)-C(215)-C(216)	0.6(2)
C(213)-C(214)-C(215)-C(218)	-178.33(14)
C(214)-C(215)-C(216)-C(211)	-1.8(2)
C(218)-C(215)-C(216)-C(211)	177.10(13)
C(212)-C(211)-C(216)-C(215)	1.8(2)
C(201)-C(211)-C(216)-C(215)	-178.32(12)
C(103)-C(102)-C(1)-O(1)	14.7(3)
C(101)-C(102)-C(1)-O(1)	-171.22(16)
Fe(1)-C(102)-C(1)-O(1)	103.73(18)

4.5 References for appendices

1 *Nomenclature of Organic Compounds* by R.B. Fox and W.H. Powell, 2nd Edition, 2001, Pub. by the American Chemical Society in conjunction with the Oxford University Press